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DETERMINATION OF THE RELATIVE VELOCITIES OF THE IONS OF SILVER NITRATE IN MIXTURES OF THE ALCOHOLS AND WATER AND ON THE CONDUCTIVITY OF SUCH MIXTURES.

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HISTORICAL SKETCH.

Such a large amount of work has been done, especially in the last few years, on the migration velocities of ions, that brief, but complete references to the investigations in this field will be given.

It was early noted that when an electric current is passed through a solution of an electrolyte, changes in concentration are produced. Faraday[1] pointed out that when an electric current is passed through a solution of an electrolyte, using copper electrodes, the solution around the cathode becomes lighter blue, while that around the anode becomes darker blue

[1] Pogg. Ann., **32**, 436 (1834).

in color. This same phenomenon was observed two years later by Gmelin,[1] and Pouillet[2] observed a similar phenomenon in a solution of a salt of gold. Smee[3] advocated the theory, put forward ten years before by Faraday, that the hydrogen from the decomposed water acted upon the copper sulphate just as another metal would do. Daniell and Miller[4] electrolyzed the sulphates of copper and zinc, and showed that the two ions in each case traveled with different velocities.

This was the state of the problem when Hittorf[5] undertook his elaborate experiments and showed conclusively that these differences in concentration were due to the differences in the velocities of the cation and the anion. Hittorf devised several forms of apparatus which, however, are the same in principle. They consist of a vertical tube divided into compartments by porous diaphragms. These diaphragms are the objectionable feature in the apparatus of Hittorf. Hittorf studied a number of questions, such as the effect of strength of current, concentration of the solutions, and temperature on the migration velocities.

The next important contribution to our knowledge in this field was that of F. Kohlrausch,[6] in which he showed that a very important relation exists between the velocities of the ions and the conductivity of solutions. In dilute solutions, under a given electromotive force, each of the ions moves through the liquid with a fixed velocity, dependent on its own chemical nature, and independent of that of the other ion. This he termed the law of the independent migration velocity of the ions. Expressed in other words, the velocity with which any ion travels is a constant for a given solvent and a given potential gradient, and is independent of the nature of the other ion or ions with which it is present in the solution. Representing the maximum molecular conductivity by $\mu\infty$ the law of Kohlrausch is formulated thus, $\mu\infty = c + a$,

[1] Pogg. Ann., **44**, 5 (1838).
[2] Compt. rend., **20**, 1544 (1845).
[3] Phil. Mag., **17**, 196 (1840).
[4] Phil. Trans., I. (1844); Pogg. Ann., **64**, 18 (1845).
[5] Pogg. Ann., **89**, 177; **98**, 1; **103**, 1; **106**, 337, 513.
[6] Wied. Ann., **26**, 1 and 145 (1879).

where c and a are the relative velocities of cation and anion, respectively.

The law of Kohlrausch has been modified by Ostwald[1] for solutions that are not completely dissociated, as follows: Representing the percentage dissociation by α, we have

$$\mu_v = \alpha(c + a).$$

It is, then, obvious that the law of Kohlrausch can be used to determine the velocity of ions. We can determine μ_v or $\mu\infty$ directly by the conductivity method, and we can determine the ratio of the two velocities by the Hittorf method. We have, then, the two equations:

$$\mu\infty = C + A; \qquad (1)$$

$$\frac{c}{a} = \frac{C}{A}. \qquad (2)$$

C and A represent the relative velocities of cation and anion at infinite dilution, and $\frac{c}{a}$ is the relative velocities as determined directly by the Hittorf method of electrolysis.

The first direct measurement of the absolute velocity of ions was made by Lodge.[2] By observing the rate at which hydrogen ions decolorize a layer of gelatine reddened by phenolphthalein, he was able to determine the rate at which the hydrogen ions moved under a given potential gradient.

The objection has been raised to the method of Lodge that the gelatine may have exerted an influence on the velocity of the ions, and, further, that the fall in potential along the tube was not regular. The agreement between the values found by Lodge and calculated by Kohlrausch shows that these sources of error could not have been serious.

Loeb and Nernst[3] devised a method for measuring the relative velocities of ions that did away entirely with the use of diaphragms. Their apparatus, which consisted essentially of a Gay-Lussac burette, and their method are open to serious objections. There is no means of properly separating the

[1] Lehrb. allg. Chem., II., 672.
[2] Brit. Assoc. Report, 1886, p. 393; 1887, p. 387.
[3] Ztschr. phys. Chem., 2, 948 (1888).

solutions after electrolysis, for the purpose of analysis, and it is much better to measure the current directly.

The method of Kistiakowsky,[1] and also that of Bein,[2] are quite similar to that of Loeb and Nernst, and the same objections apply to the latter as to the former.

Whetham[3] measured the absolute velocities of certain ions, avoiding the use both of diaphragms and gelatine solutions. He measured the velocity of the moving boundary between two solutions containing a common ion, one of the solutions being colored.

Schrader[4] devised a form of apparatus for determining migration velocities, which was essentially a modification of that used by Kistiakowsky. His apparatus, however, was bent in such a form that he could draw the solution off from either electrode, directly, for analysis.

Certain objections apply to all the methods thus far discussed for determining the migration velocities of ions. The earlier investigators either separated the solutions around the electrodes by means of porous diaphragms, or relied upon the difference in specific gravity resulting from the electrolysis to secure a separation.

Some of the objections to the earlier methods were removed by a form of apparatus devised by Jones and Mather.[5] The new feature of this was that it provided a means of separating completely the two solutions around the electrodes after the electrolysis was ended. The apparatus consists essentially of two vertical limbs united by a U-tube. At the bottom of the U-tube is a stop-cock, of large bore so as not to offer too much resistance to the passage of the current. The electrodes were introduced through ground-glass stoppers inserted into the bottoms of the upright tubes. After the electrolysis was ended the stop-cock was turned, and thus the portions of the solution on the two sides of the apparatus

[1] Ztschr. phys. Chem., **6**, 97 (1890).
[2] Wied. Ann., **46**, 29 (1892).
[3] Phil. Trans., A, 337 (1893).
[4] Ztschr. Elektrochem., **3**, 498 (1896).
[5] This JOURNAL, **26**, 473 (1901).

were completely separated. Each side could then be carefully washed out and the solution analyzed.

Mather worked on solutions of silver nitrate in alcohol, and found, as others had done in aqueous solutions, that with rise in temperature the velocities of cation and anion tended to become equal.

Since the above investigation was carried out in this University a number of pieces of work have been done on migration velocities. Gordon[1] studied the effect of change in temperature, especially with cadmium salts.

Hopfgartner's[2] work was similar in character to that of Schrader.

Kummel's[3] method is similar to that employed by Lodge.

The most elaborate investigation in the field that we are now considering, since the time of Hittorf, is that of Bein.[4] He described in all five forms of apparatus with various means of separating the solution around the cathode from that around the anode. In one form he used essentially the method described by Loeb and Nernst; in another the solutions are separated by a column of mercury. In general, it may be said that the apparatus devised and used by Bein is very complex, and in some cases probably much more so than necessary.

The next work to be considered in this connection is that of O. Masson,[5] who devised and used a new form of apparatus for measuring absolute velocities. Two flasks, each provided with a lateral opening, are connected by a graduated horizontal tube containing a mixed solution of gelatine and the salt to be investigated. Both anode and cathode solutions must be distinctly colored, the colored ion being the cation in the anode solution and the anion in the cathode solution. Further, the colored ions must migrate at a slower rate than the corresponding ions of the salt in the tube. A suitable anode solution is copper sulphate with a copper anode. A

[1] Ztschr. phys. Chem., **23**, 469 (1897).
[2] *Ibid.*, **25**, 115 (1898).
[3] Wied. Ann., **64**, 655 (1898).
[4] Ztschr. phys. Chem., **27**, 54 (1898); **28**, 439 (1899).
[5] *Ibid.*, **29**, 501 (1899); Phil. Trans., A, **192**, 331.

suitable cathode solution is sodium chromate with a platinum cathode.

When the current passes, the progress of the cation in the colorless solution in gelatine is accompanied by an equal advance in the blue copper ions. The colorless anions in the gelatine are, similarly, followed by the yellow chromium ions. The contents of the tube thus become blue at one end, colorless in the middle, and yellow at the other end. The relative lengths of the blue and yellow parts give the relative velocities of the cation and anion.

The relative velocities of the ions thus obtained are compared with Kohlrausch's values, and a fair agreement was found to exist. The absolute velocities in gelatine are somewhat smaller than in aqueous solution.

About this time Kohlrausch published an investigation on the velocities of ions in dilute aqueous solutions at 18°, and up to a concentration of one-tenth normal. He showed that, for solutions of from one-twentieth to one-tenth normal, the conductivities of compounds composed of univalent ions, or of univalent ions in combination with bivalent ions, may be calculated from the ionic velocities. This does not hold for compounds composed of bivalent ions only, since, for such the velocities vary with increasing concentration.

Among the later investigations on this subject is that of Steele.[1] The method which he employed is in principle similar to that used by Masson. The aqueous solution is imprisoned between partitions of gelatine containing the indicator ion in solution. The method of Steele, however, differs from that of Masson in two respects. The measurements of the relative velocities are made in water and not in gelatine, and the employment of a colored ion is not necessary. All that is required is that a solution of the indicator containing about the same number of gram-molecules per liter as the solution of salt whose ionic velocities are to be measured, should differ from the latter in density and refractivity. The choice of indicators is thus very largely increased. The results obtained

[1] J. Chem. Soc., 79, 414 (1901).

by this method agree very well with those found by other good methods.

A form of apparatus which differs very appreciably from that used by any previous investigator was designed and used by A. A. Noyes.[1] It consists essentially of two U-tubes attached by rubber tubing. The two arms of each tube are of unequal lengths, and the electrodes are inserted into the longer arms. The electrodes are of platinum, and the acid and alkali formed around the electrodes are titrated from burettes passing through stoppers into the longer arms of the U-tubes. By means of this apparatus, Noyes was able to measure the relative velocities of the ions of such salts as potassium chloride, sodium chloride, etc.

Thus far no work had been done in very dilute solutions, and it was important that this condition, especially, should be investigated. Jahn[2] and his pupils used a form of apparatus resembling in some respects that employed by Noyes. It consisted of a vessel of the form of an Erlenmeyer flask, connected with a U-tube, which, in turn, was connected with a larger part of the apparatus, whose size could be varied according to the dilution of the solution to be used. With their apparatus they measured the relative velocities of a few acids and quite a number of salts. They studied the effect of dilution upon the relative velocities of the ions, and found in many cases that the relative velocities did not become constant until a dilution of between 200 and 300 liters was reached.

Up to this time there was still a sharp limit in the dilution at which measurements of relative velocities had been made. This applies also to the work of Jahn, Noyes, and Bein. Jahn could not obtain accurate results above a dilution of 150 liters, and this dilution is not sufficient to measure the velocities of the ions of many salts.

Steele and Denison[3] undertook to measure the velocities of ions at dilutions comparable with those at which accurate

[1] Ztschr. phys. Chem., **36**, 61 (1901).
[2] *Ibid.*, **37**, 673 (1901).
[3] J. Chem. Soc., **81**, 456 (1902).

conductivity measurements could be made, and also to test whether, at such dilutions, the relative velocities would become constant. Salts of calcium were employed because satisfactory conductivity measurements had been made to a high dilution. At a dilution of 300 or 400 liters a large volume of the solution must be subjected to electrolysis in order that an appreciable quantity of the salt would be carried by the current. With this idea in mind, they devised a form of apparatus which admits of the electrolysis of a large volume of the solution. A W-shaped tube was connected with a reservoir to which fresh quantities of the solution could be added as that in the apparatus was drawn off. The solution on each side of the apparatus could be drawn off separately, the apparatus refilled, and the electrolysis allowed to proceed until several liters of solution had passed through the apparatus. They worked with a number of salts, including potassium chloride.

The values which they found for potassium chloride agree with the best results obtained by other investigators, and confirm Kohlrausch's assumption as to the constancy of migration velocities of the ions of salts of this class with increasing dilution.

Steele[1] continued the above investigation, using such salts as barium chloride and magnesium sulphate. He concluded that the velocity is not independent of the concentration, and that the velocity of the cation varies with the salt that is used. He explained the change in velocity with the concentration as due to the formation of complex ions in solution. This would mean a motion of at least a part of the undissociated salt along with the ions.

Abegg and Gauss[2] studied the effect of the initial concentrations of the neighboring electrolytes, and recommended that the concentration of the indicator jelly should be at least equivalent to that in the solution of the electrolyte under investigation.

The effect of electrical endosmose on transport numbers was investigated by Denison.[3] His method was essentially

[1] Phil. Trans., A., 198 (1901).
[2] Ztschr. phys. Chem., 40, 737 (1902).
[3] *Ibid.*, 44, 575 (1903).

that employed by Steele. In this investigation he studied also the effect of gelatine on the transference numbers. He found that so long as the gelatine was liquid, it exerted no influence on the transference numbers. In solid gelatine the velocity of the cation is diminished relative to that of the anion. A similar phenomenon is observed in very concentrated aqueous solutions, and it is highly probable that in both cases the specific frictional coefficient of the ions, as well as the formation of complex ions, play an important part.

Denison considers it probable that the gelatine combines with certain salts, forming complex cations. He also points out that various proteids have the power of combining with acids and alkalies, forming salt-like compounds.

It is thus very probable that gelatine, or some product of its hydrolysis, combines with the substance dissolved in it. This would explain the above difference in the transport numbers in liquid and solid gelatine.

Very little work has been done even up to the present on migration velocities in any solvent other than water. A few determinations have already been referred to, but they are very few in number. Still less has been done on transference numbers in mixed solvents.

Carrara[1] carried out an investigation on the migration velocities of ions in solutions in methyl alcohol. He worked with quite a number of salts, using three different forms of apparatus: One contained a membrane, and was similar to one of the forms used by Hittorf; another was the apparatus of Loeb and Nernst, while the third he describes as a new form of apparatus. This last form is a very slight modification of that devised and used by Jones and Mather in this University seven years ago. No mention is made by Carrara of this fact, doubtless due to an oversight on his part.

He brings out an interesting point in connection with lithium chloride. His results indicate the existence of complex ions in a solution of this salt, which is a binary electrolyte.

[1] Gazz. chim. ital., **33**, I., 241 (1903).

On comparing the transport numbers found by Carrara in aqueous and methyl alcohol solutions, it is seen that the difference between them is very small, and of the same order of magnitude as the differences obtained by a change in concentration. In general, the transport number for the anion in methyl alcohol is higher than in water.

From these considerations he draws the conclusion that the transport numbers for the ions of an electrolyte tend towards the same value, independent of the solvent in which the electrolyte is dissolved. In other words, if the dilution is sufficiently great and no secondary reactions take place, the transport numbers of an electrolyte are the same in all solvents. The transport numbers found for solutions of salts in methyl alcohol are the same as in aqueous solutions at greater concentrations.

The most recent investigations in the field of migration velocities are those of Huybrechts[1] and of Wolff.[2] They used a form of apparatus which was a slight modification of that formerly employed by Jahn and his pupils.

As has already been stated, in most of the investigations aqueous solutions have been dealt with, and comparatively little work has been done in solvents other than water. The only investigations that have been carried out in any other solvent were those of Lenz, Mather, and the recent work of Carrara.

EXPERIMENTAL PART.

This investigation was undertaken for the purpose of determining what effect mixtures of methyl alcohol and water would have on the relative velocities of the ions of such a salt as silver nitrate.

The work of Jones and Lindsay[3] on the conductivity of certain salts in water, methyl, ethyl, and propyl alcohols, and mixtures of these solvents suggested this work.

In their work, Jones and Lindsay found that the conductivities of such salts as potassium iodide, ammonium bromide,

[1] Dissertation, University of Berlin, 1902.
[2] *Ibid.*, 1903.
[3] This JOURNAL, **28**, 329 (1902).

strontium iodide, etc., were less in mixtures of the solvents than in either of the solvents alone. Especially was this the case in mixtures of methyl alcohol and water. Considering these facts, the first thing to determine was whether silver nitrate would give similar conductivity results, and if so, whether there was any relation between this phenomenon and the relative velocities. The conductivities of silver nitrate in these solvents and varying mixtures of them were determined. The water, methyl and ethyl alcohol, were purified by the methods described by Jones and Lindsay. In each case a mother solution was made in the solvent in question, and the remaining solutions were obtained by successive dilutions with some of the solvent of the same composition. In this way an error was avoided which would result from the contraction when alcohol and water were mixed, and also prevent the accompanying heat effect. In some cases, as in very dilute solutions, where such small quantities of the mother solution were required, a second mother solution was made from the first, and the more dilute solutions made from it in the way described. The strength of these mother solutions was determined by titrating with a standard solution of ammonium sulphocyanate.

Conductivity Apparatus Employed.

The apparatus described and used was similar to that employed by Jones and Lindsay. The cells differed from the ordinary Arrhenius cell, being provided with a ground-glass top to prevent evaporation of the more volatile solvents, and also protect the anhydrous alcoholic solutions from the moisture of the baths and air. The glass tubes carrying the electrodes were passed through thin rubber tubes in the cap. Sealing-wax was then run over the outside of the joint.

The zero-bath was prepared as follows: A large glass battery-jar was filled with finely crushed ice and distilled water. It was then placed in a water-bath and the space between filled with finely crushed ice and water. This proved very efficient, as it was possible to keep within 0°.05 of zero for hours. The bath at 25° was of the ordinary form, and was

kept in constant motion by a stirrer driven by means of a hot-air engine. The thermometers used could be accurately read to 0°.02. The burettes and flasks were carefully calibrated.

Conductivity Measurements.

All the conductivity measurements were made at the two temperatures, 0° and 25°. In the following tables v = number of liters of solution containing a gram-molecular weight of the salt; $\mu_v 0°$ = molecular conductivity at 0°; $\mu_v 25°$ = molecular conductivity at 25°:

Table I.—Molecular Conductivity of Silver Nitrate in Water.

v.	μ_v 0°.	μ_v 25°.
10	55.72	99.46
20	58.63	105.72
40	63.10	110.22
80	63.16	115.81
160	65.38	119.86
320	69.91	125.08
640	71.05	125.86
1280	70.59	125.35

Table II.—Molecular Conductivity of Silver Nitrate in Ethyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
9.71	7.11	....
19.43	8.90	14.26
38.86	11.35	16.96
77.73	13.10	20.11
155.47	15.13	23.87
310.95	17.04	26.46
621.89	19.43	30.62

Table III.—Molecular Conductivity of Silver Nitrate in Methyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
10	25.96	35.77
20	32.63	44.67
40	39.71	53.42
80	45.28	62.95
160	51.09	70.36
320	56.71	80.17
640	61.42	88.22

Table IV.—Molecular Conductivity of Silver Nitrate in 25 Per Cent Ethyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
38.86	25.95	59.70
77.73	26.65	62.75
155.47	26.45	63.82
310.95	28.72	64.87
621.89	28.84	68.28

Table V.—Molecular Conductivity of Silver Nitrate in 50 Per Cent Ethyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
19.43	15.25	37.87
38.86	15.81	39.50
77.73	17.04	42.42
155.47	17.92	45.15
310.95	19.10	47.13
621.89	19.90	49.39
1243.78	20.79	52.80

Table VI.—Molecular Conductivity of Silver Nitrate in 75 Per Cent Ethyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
19.43	13.12	27.01
38.86	14.30	30.43
77.73	16.79	33.65
155.47	19.48	35.94
310.95	18.00	39.01
621.89	19.41	40.14

Table VII.—Molecular Conductivity of Silver Nitrate in 25 Per Cent Methyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
40	35.63	72.68
80	36.95	75.56
160	39.03	79.34
320	41.03	82.93
640	41.23	83.91

Table VIII.—Molecular Conductivity of Silver Nitrate in 50 Per Cent Methyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
20	27.27	53.33
40	28.63	56.80
80	29.93	59.75
160	31.47	63.22
320	32.29	65.85
640	34.67	68.67

Table IX.—Molecular Conductivity of Silver Nitrate in 75 Per Cent Methyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
20	27.98	48.20
40	30.03	52.33
80	32.81	57.17
160	35.22	61.31
320	35.71	63.23
640	40.27	69.42

Table X.—Temperature Coefficients of Conductivity of Silver Nitrate in Water (0° to 25°).

v.	Temperature coefficient.
10	1.75
20	1.88
40	1.88
80	2.10
160	2.14
320	2.21
640	2.20
1280	2.19

Table XI.—Temperature Coefficient of Conductivity of Silver Nitrate in Ethyl Alcohol (0° to 25°).

v.	Temperature coefficient.
19.43	0.214
38.86	0.224
77.73	0.280
155.47	0.350
310.95	0.377
621.89	0.488

Table XII.—Temperature Coefficient of Conductivity of Silver Nitrate in Methyl Alcohol (0° to 25°).

v.	Temperature coefficient.
10	0.392
20	0.482
40	0.548
80	0.707
160	0.771
320	0.938
640	1.702

Table XIII.—Temperature Coefficients of Conductivity of Silver Nitrate in Mixtures of Ethyl Alcohol and Water of Various Compositions.

	Temperature coefficients.		
v.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.
19.43	....	0.905	0.556
38.86	1.35	0.962	0.645
77.73	1.44	1.015	0.674
155.47	1.49	1.089	0.658
310.95	1.45	1.121	0.840
621.89	1.58	1.180	0.829
1243.78	....	1.280	....

Table XIV.—Temperature Coefficients of Conductivity of Silver Nitrate in Mixtures of Methyl Alcohol and Water of Various Compositions.

	Temperature coefficients.		
v.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.
20	....	1.04	0.810
40	1.48	1.13	0.892
80	1.54	1.19	0.974
160	1.61	1.27	1.024
320	1.68	1.34	1.100
640	1.71	1.36	1.166

In order to see the connection existing between the conductivities in each solvent, the following tables are given for comparison :

Table XV.—Comparison of the Molecular Conductivities of Silver Nitrate in Ethyl Alcohol and Mixtures of It with Water at 25° C.

v.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.	One hundred per cent alcohol.
19.43	....	37.87	27.01	14.26
38.86	59.70	39.50	30.43	16.96
77.73	62.75	42.42	33.65	20.11
155.47	63.82	45.15	35.94	23.87
310.95	64.87	47.13	39.01	26.46
621.89	68.28	49.39	40.14	30.62

It is seen from these values that the molecular conductivity in ethyl alcohol and mixtures with water does not show a minimum in the ordinary range of dilution, but still does not obey the law of mixtures. This is in accordance with Jones and Lindsay's work on potassium iodide. In that case they did not find a trace of a minimum at 25°.

The values in Table XV. are plotted as curves in Fig. I.,

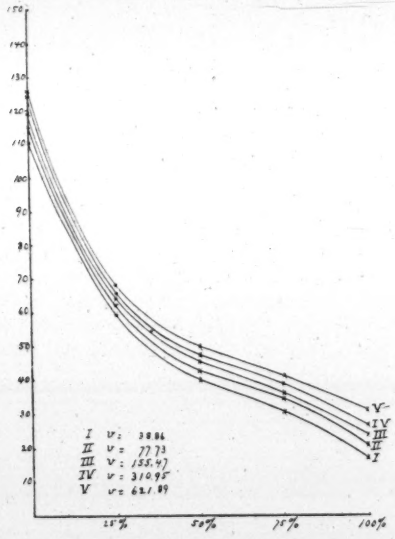


Fig. I.

the abscissae representing the different per cents of alcohol, and the ordinates the molecular conductivities.

Table XVI.—Comparison of the Molecular Conductivities of Silver Nitrate in Ethyl Alcohol and Mixtures of It with Water at 0° C.

v.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.	One hundred per cent alcohol.
9.71	....	....	....	7.11
19.43	....	15.25	13.12	8.90
38.86	25.95	15.81	14.30	11.35
77.73	26.65	17.04	16.79	13.10
155.47	26.45	17.92	19.48	15.13
310.95	28.72	19.10	18.00	17.04
621.89	28.84	19.90	19.41	19.43
1243.78	....	20.79	....	....

These values are plotted in Fig. II. The curves are of the same general form as in Fig. I. No distinct minimum is shown, but the form of the curve indicates that a minimum value is approached.

Table XVII.—Comparison of the Molecular Conductivities of Silver Nitrate in Water, Methyl Alcohol, and Mixtures of These Solvents at 25° C.

v.	Water.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.	One hundred per cent alcohol.
10	99.46	....	....	....	35.77
20	105.72	....	53.33	48.20	44.67
40	110.22	72.68	56.80	52.33	53.42
80	115.81	75.56	59.75	57.17	62.95
160	119.86	79.34	63.22	61.31	70.36
320	125.08	82.93	65.85	63.23	80.17
640	125.86	83.91	68.67	69.42	88.22
1280	125.35	....	....	....	....

These values are plotted in Fig. III. In nearly every case the minimum, as shown by the curve, lies between mixtures of the solvents containing respectively 50 and 75 per cent of alcohol.

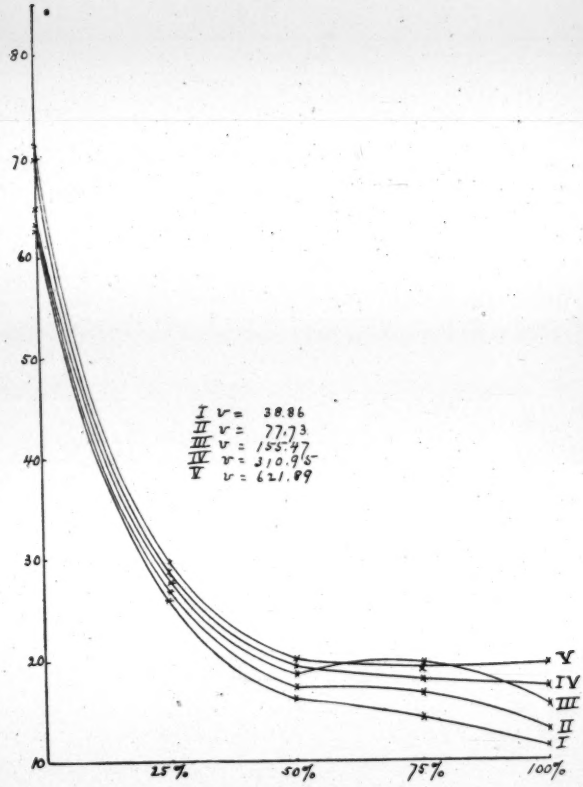

80
70
60
50
40
30
20
10
25%
50%
75%
100%
I v = 38.86
II v = 77.73
III v = 155.47
IV v = 310.95
V v = 621.89
V
IV
III
II
I

Fig. 11.

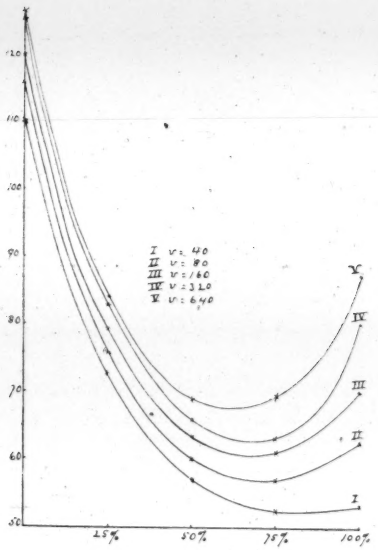


Fig. III.

Table XVIII.—Comparison of the Molecular Conductivities of Silver Nitrate in Water, Methyl Alcohol, and Mixtures of These Solvents at 0° C.

v.	Water.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.	One hundred per cent alcohol.
10	55.72	....	....	....	25.96
20	58.63	....	27.27	27.98	32.63
40	63.10	35.63	28.63	30.03	39.71
80	63.16	36.95	29.93	32.81	45.28
160	65.38	39.03	31.47	35.22	51.09
320	69.91	41.03	32.29	35.71	56.71
640	71.05	41.23	34.67	40.27	61.42
1280	70.59	....	....	....	....

These results are plotted in Fig. IV. The curves are of

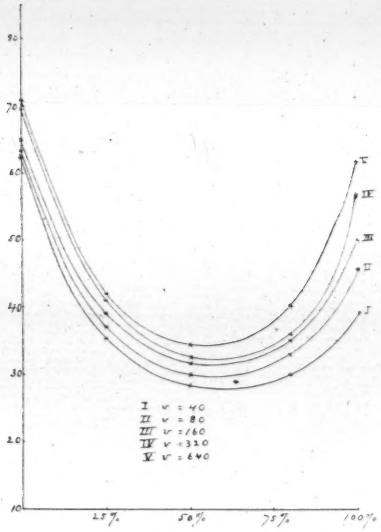


Fig. IV.

the same general form as the curves in Fig. III. They differ, however, in some respects. The chief difference is that the minimum point has shifted to the left, corresponding now to an alcohol-water mixture not far from 50 per cent.

From the above results it is clear that silver nitrate is not an exception to the general relation found by Jones and Lindsay. It was now interesting to see what effect alcohol would have upon the relative velocities of the ions, especially in the mixtures of methyl alcohol and water. This case seemed to offer a good field for investigation. Therefore, this particular part of the problem was taken up, and a few determinations of relative velocities were made in ethyl alcohol.

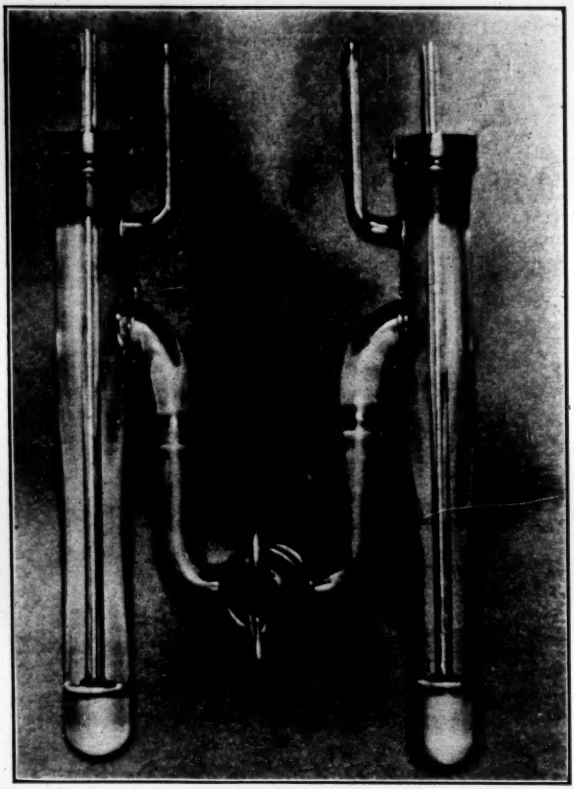


Plate I.

Relative Velocities of Ions.

In the last few years a large number of investigations have appeared on the relative velocities of ions. Most of them, however, have had to deal with aqueous solutions of a large number of substances. Few have determined the relative velocities in methyl and ethyl alcohol, and practically nothing has been done upon mixtures of these solvents.

In most of the later investigations new forms of apparatus have been devised, many of them being very complicated. The question arises whether such a high degree of complexity is necessary for effecting the electrolysis and separation of the solutions. In many of the new forms no special means were provided for the final separation of the solutions, some depending simply upon the difference in specific gravities of the solutions resulting from the electrolysis. Discrepancies in the results are, therefore, probably due in part to the incomplete separation of the two portions of the solution. But one form has been described which prevents diffusion. This apparatus was devised by Jones and Mather, in this University, and has already been fully described.

From an examination of the different forms of apparatus, that used by Mather seemed best adapted for this investigation, but some very serious difficulties, pointed out in part by Mather in his paper, had to be overcome. These difficulties, however, were avoided by devising the apparatus shown in Plate I.

The two limbs are 20 cm. long and 2 cm. in diameter, with the electrodes inserted from the top through ground-glass stoppers. Just below the stoppers two small tubes are attached, which extend outward and upward, the vertical part being graduated in millimeters. The lower part of this small tube is 5 mm. in diameter, and the vertical part is about 3 mm.

The limbs are connected, 3 cm. below the stoppers, by a U-tube 1.5 cm. in diameter, in the same plane with the limbs. The bottom of the U-tube is 5 cm. above the lower ends of the limbs. At the center of the U-tube is a stop-cock of 8 mm.

bore. The electrodes were made of pure, round, silver plates, into which a platinum wire was riveted in order to seal them into glass tubes running through the ground-glass stoppers. The small amount of platinum exposed in the bottom of the silver plate was covered by a thin coating of fusion glass. The glass tubes were then firmly secured in the ground-glass stoppers by means of a piece of black rubber tubing, which was placed on the tube and through which it was forced. The electrical connection was then made by filling the tubes with mercury, which made connection with the silver plate by means of the platinum wire riveted into the plate, as was stated above.

This form of apparatus could easily be placed in a thermostat on hooks arranged for that purpose, which supported the apparatus under the U-tube.

In order to keep a constant temperature, the thermostat-bath represented in Plate II. was constructed. This proved to be very efficient, remaining constant to within 0°.1, and at the same time affording plenty of room for three pieces of apparatus and voltameters. It consists of a wooden box 2 feet long, 14 inches wide, and 10 inches deep, lined inside with heavy galvanized iron. The iron lining extends to within one-half an inch of the top of the wooden box. One and one-half inches from the top of the box a heavy, movable shelf was arranged in which the three voltameters could be placed and kept at a constant temperature. In the bottom of the wooden box a hole 14 inches square was lined only with metal, so that a small flame could be applied. Hooks were arranged on the side of the bath opposite the shelf for the voltameters, and for the apparatus represented in Plate I., which was suspended from them. The bath was then filled with water to the level of the shelf and kept at constant temperature by means of an Ostwald thermoregulator. In order to secure a uniform temperature the water in the bath was kept in constant motion by a stirrer, which was driven by a small hot-air engine. For determinations at 0° the bath was filled with finely broken ice, and the apparatus placed in the bath in the same manner as in the 25° bath. The wooden casing of the bath,

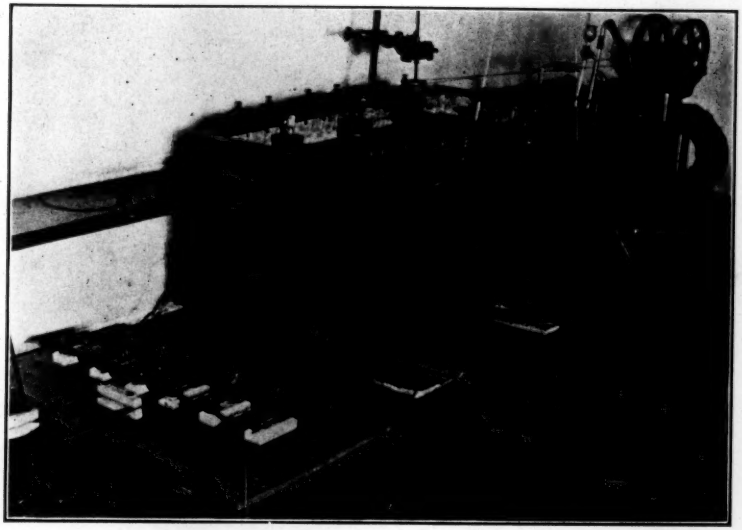


Plate II.

in determinations at this temperature, serves as a poor conductor of heat. All of the electrical connections attached to the bath were placed upon a block of hard rubber to prevent any leak of current.

Special precautions were also taken in all the wiring about the bath. Flexible insulated wire was used, and wherever two wires crossed additional precaution was taken to run them through rubber tubing. The box was also covered thickly with shellac as an additional precaution. Two currents of different strengths were used. One current of 60 volts was supplied by a storage battery. The other current of 110 volts was supplied directly from the power house. In every case the current was measured by means of a voltameter, consisting of platinum crucibles and pure silver anodes. The platinum crucibles were placed in weighing-flasks to insulate them entirely from each other, and, at the same time, to serve as a convenient means of placing them upon their supports in the constant-temperature bath. Connections with the circuit were made by placing the platinum crucible upon a copper plate to which a wire had been soldered.

The anode of pure silver was suspended in the platinum crucible by running it through a rubber stopper, which fitted the weighing-glass and also served as a cover to it. The silver anode was also inserted into a clean linen bag to prevent any small particles, which become detached from the anode, from falling into the crucible and therefore being weighed with the silver deposited by the current.

The platinum crucibles were treated with fused acid potassium sulphate, then boiled with nitric acid, heated in the flame of the blast-lamp, cooled in a desiccator, and weighed before each experiment. The deposit formed by the current was treated in accordance with the directions recommended by Richards[1] in his investigation upon the determination of the chemical equivalent of copper and silver.

Preparation of Solutions.

The analysis in every case was made by titration with am-

[1] Ztschr. phys. Chem., 41, 302 (1902).

monium sulphocyanate, ferric ammonium sulphate being used as the indicator. Special care was taken in the preparation of the solutions, and their strength was determined by titration with standard solutions of potassium chloride.

In the preparation of the solutions of potassium chloride the pure salt, which had been purified especially for conductivity work, was used. Small amounts of this salt were weighed and dissolved in water. It was then titrated against the silver nitrate. The silver nitrate used was Kahlbaum's best material, which was free from any detectable impurities.

The water employed in the preparation of the solutions was obtained by redistillation of ordinary distilled water, essentially by the method described by Jones and Mackay.[1] The ordinary distilled water, to which a solution of chromic acid had been added, was boiled, and the steam passed through a boiling solution of barium hydroxide.

The absolute alcohol was prepared by distillation from quicklime, further dehydrated with anhydrous copper sulphate, and finally distilled from a small amount of sodium just before using. In the preparation of the solutions in absolute alcohol the following method was adopted: The silver nitrate was placed in a dry measuring-flask. The latter was filled with alcohol, by means of a siphon, from the bottle containing the alcohol which had been distilled from sodium. The alcohol was thus not allowed to come in contact with moisture. The bottle was closed by a two-hole rubber stopper. Through one hole the siphon passed, and through the other the drying-tube which permitted the air to enter the flask. The siphon led to a Gooch funnel, which was also closed with a two-hole rubber stopper; the siphon passed through one hole and another drying-tube through the other one. The funnel was connected with the measuring-flask and alcohol siphoned into it. The resulting solution of silver nitrate was then removed to a dry bottle which was closed with a rubber stopper, connection with the interior being made by a glass tube and drying-tube.

When it was desired to draw off part of the solution either

[1] This JOURNAL, 19, 91 (1897).

for analysis or to fill the apparatus, the point of a burette was connected with the glass tube in the bottle by means of a rubber tube, and the solution was drawn up into the burette by aspiration through a drying-tube which closed its upper end. The burette was then connected with one of the small graduated tubes on the apparatus, the other one being closed by a Bunsen valve. The two small tubes were connected and the apparatus tilted first one way and then the other in order to remove the last trace of air from beneath the stoppers. Each tube was then closed with a Bunsen valve, and the apparatus placed in the constant-temperature bath. The connections with the circuit and voltameter being made, the electrolysis was begun.

Calibration of Apparatus.

The first calibration of the apparatus was by weighing first the empty apparatus, then, with one side full of water, and finally with both sides full. In this way the exact contents of the apparatus could not be determined, but the ratio between the two sides could be obtained.

The second and subsequent calibrations were made by measuring the contents of each side with a burette, which had previously been calibrated by means of the apparatus designed by Morse and Blalock.[1]

Calibration No. 1, December 7, 1903.

Apparatus No. 1 :	
Weight of empty apparatus	287.95
" " apparatus with left side full of water	356.325
Weight of apparatus full of water	423.675
Therefore, right side contains	49.623 per cent
" left side contains	50.377 "
Apparatus No. 2 :	
Weight of epmty apparatus	265.52
" " apparatus with left side full of water	330.91
Weight of apparatus full of water	396.50
Right side contains	49.924 per cent
Left " "	50.076 "

[1] This JOURNAL, **16**, 479 (1894).

Apparatus No. 3 :

Weight of empty apparatus	267.79
" " apparatus with left side full of water	329.95
Weight of apparatus full of water	390.77
Right side contains	49.455 per cent
Left " "	50.545 "

Calibration No. 2, January 11, 1904.

Apparatus No. 1 :

Contents of right side	67.71 cc.
" " left "	68.73 "
Right side contains	49.616 per cent
Left " "	50.384 "

Apparatus No. 2 :

Contents of right side	65.39 cc.
" " left "	65.21 "
Right side contains	50.07 per cent
Left " "	49.93 "

Apparatus No. 3 :

Contents of right side	62.44 cc.
" " left "	63.34 "
Right side contains	49.485 per cent
Left " "	50.515 "

Calibration No. 3, February 15, 1904.

Apparatus No. 1 :

Contents of right side	68.43 cc.
" " left "	68.61 "
Right side contains	49.934 per cent
Left " "	50.066 "

The position of electrodes in this apparatus was changed just before the calibration.

Apparatus No. 2 :

Contents of right side	65.82 cc.
" " left "	65.42 "
Right side contains	50.114 per cent
Left " "	49.886 "

Apparatus No. 3 :

Contents of right side	62.30 cc.
" " left "	63.64 "
Right side contains	49.468 per cent
Left " "	50.532 "

Calibration No. 4, March 21, 1904.

Apparatus No. 1 :	
Contents of right side	68.56 cc.
" " left "	68.66 "
Right side contains	49.963 per cent
Left " "	50.037 "
Apparatus No. 2 :	
Contents of right side	66.10 cc.
" " left "	65.85 "
Right side contains	49.447 per cent
Left " "	50.533 "
Apparatus No. 3 :	
Contents of right side	62.45 cc.
" " left "	63.85 "
Right side contains	49.447 per cent
Left " "	50.553 "

Measurement of Relative Velocities.

Knowing the relation between the two sides of the apparatus, the experiments were carried out as follows : The apparatus was filled from the burette, as described above, to the zero mark on each side. The open ends of the small leveling limbs were then closed by Bunsen valves, and the whole placed in the bath by supporting it on hooks arranged for that purpose. The water in the bath and the solution in the apparatus were practically the same height, as the apparatus was immersed until the bottom of the ground-glass stoppers were on a level with the surface of the water.

Connection with the circuit and voltameters being made, the electrolysis was allowed to proceed until enough silver was deposited in the voltameters to be weighed accurately, the deposit usually weighing between 0.05 to 0.10 gram. The time of the electrolysis depended upon the resistance offered by the solution. At the close of the electrolysis the apparatus was removed from the bath, and the level of the solution in the apparatus brought to corresponding graduations on each leveling-tube. The stop-cock was then closed and the contents were carefully washed, filtered through glass wool or washed asbestos to remove any disintegrated

silver, made up to a known volume, and analyzed. The accuracy of the results was determined by comparing the amount of silver found on analysis with that calculated from the amount of solution placed in the apparatus at the beginning of the experiment. With this data the relative velocities of the ions could easily be calculated as follows: The amount of silver found in the apparatus as a whole was multiplied by the per cent contained on the side that increased, thus giving the amount of silver contained on that side at the beginning of the experiment. This was then subtracted from the amount found on that side by analysis, which gave the amount of increase due to electrolysis. This increase was then divided by the weight of the silver deposited in the voltameter, the result being the relative velocity of the anion. The strength of the current in no case exceeded 0.005 ampere.

Silver Nitrate in Water.

In these determinations the apparatus was filled, and the experiment carried out as described above. After the electrolysis each side was carefully washed out, filtered through glass wool, and diluted to 200 cc. Aliquot parts of this were then taken and titrated against a standard solution of ammonium sulphocyanate. At the beginning of this investigation the titrations of several of the determinations were made with N/10 ammonium sulphocyanate, but it was soon found that this was too concentrated to give good results, since the burette could not be read with sufficient accuracy to obviate a large experimental error. Another very serious difficulty was that in titrating such a strong solution against a comparatively weak one, in many instances, the smallest fraction of a drop that could be used would go considerably beyond the neutral point.

To prevent these experimental errors the titrations were made with a N/25 solution of ammonium sulphocyanate. With a solution of this strength the point of change could easily be distinguished, and the error in reading the burette would be diminished, since a larger volume of solution would be used. The results of these determinations are given in

the following table. In this, as in all subsequent tables, the following symbols will be used:

t = temperature of the bath.

m = concentration of the solution in gram-molecular weights per liter.

c = change in concentration expressed in number of cubic centimeters of N/10 silver nitrate.

v = amount of silver in grams, deposited in the voltameter.

a = velocity of the anion.

Table XIX.—Relative Velocity of the Anion of Silver Nitrate in Water at 25°.

t.	*m.*	*c.*	*v.*	*a.*
25°	0.1	20.964	0.4320	0.5238
25°	0.1	20.034	0.4126	0.5260
25°	0.1	12.705	0.2622	0.5230
25°	0.1	12.452	0.2535	0.5301
25°	0.1	13.008	0.2587	0.5387

Values obtained by other observers, although at different temperatures, are given in the following table:

Table XX.—Relative Velocity of the Anion of Silver Nitrate Determined by Other Observers in Aqueous Solution at Different Temperatures.

t.	*m.*	*a.*	
29°.1	0.1	0.5317	Mather
45°	0.025	0.5246	"
47°.7	0.1	0.5280	"
47°.9	0.1	0.5272	"
47°.4	0.1	0.5286	"
19°	0.118	0.526	Hittorf
19°	0.055	0.526	"
19°	0.024	0.526	"
20°	0.1043	0.528	Nernst and Loeb
26°	0.0521	0.524	" " "
26°	0.0230	0.522	" " "
26°	0.0105	0.523	" " "

Table XXI.—Relative Velocity of the Anion of Silver Nitrate in Aqueous Solution at 0° C.

m.	*c.*	*v.*	*a.*
0.102	6.3370	0.1214	0.5633
0.102	6.4940	0.1229	0.5622
0.102	6.2480	0.1198	0.5629

Table XXII.—Relative Velocity of the Anion of Silver Nitrate as Determined by Other Observers in Aqueous Solution at 0°.

m.	
0.1	0.5414 Mather
0.1	0.5401 "
0.1	0.5413 "
0.025	0.5377 "
0.025	0.5380 Nernst and Loeb

These values differ considerably from those obtained in this investigation at the same temperature. In the determination of the first three by Mather, he measured the current with a d'Arsonval galvanometer, and by this means only determined the average strength of the current, thus probably introducing a considerable experimental error.

In the last two determinations in Table XXII. the current in both cases was measured by a silver voltameter, but the concentration of the solution was less, and, as is well known, a decrease in concentration diminishes the relative velocity of the swifter ion.

Table XXIII.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at 25° C.

m.	*c.*	*v.*	*a.*
0.1012	2.893	0.0510	0.6122
0.0763	5.584	0.1021	0.5903
0.0763	5.580	0.1013	0.5945
0.0784	5.343	0.0942	0.6121
0.094	3.625	0.0663	0.5903
0.094	4.617	0.0840	0.5932

The solutions of silver nitrate in ethyl alcohol offered great resistance to the current, and where the large changes in concentration were obtained the current was allowed to run for ten or twelve hours.

Table XXIV.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 25° C.

m.	*c.*	*v.*	*a.*
0.100	8.964	0.1655	0.5849
0.100	8.971	0.1684	0.5800
0.100	8.222	0.1517	0.5849
0.098	5.891	0.1098	0.5789
0.098	5.726	0.1086	0.5700

A much larger change in concentration was obtained in these determinations than in those in ethyl alcohol, because the silver nitrate was considerably more soluble in methyl than in ethyl alcohol, and thus the electrolysis could proceed further without danger of the determination being lost on account of the cathode and anode liquids becoming mixed.

Table XXV.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 0°.

m.	*c.*	*v.*	*a.*
0.097	3.4570	0.0639	0.5823
0.097	3.8530	0.0722	0.5898
0.096	3.1447	0.0572	0.5933
0.096	2.2730	0.0422	0.5861
0.096	3.0962	0.0572	0.5842

Table XXVI.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 25 Per Cent Methyl Alcohol and Water at 25°.

m.	*c.*	*v.*	*a.*
0.1	6.6280	0.1285	0.5567
0.1	6.4530	0.1258	0.5536
0.1	6.2880	0.1231	0.5513

Table XXVII.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 25 Per Cent Methyl Alcohol and Water at 0°.

m.	*c.*	*v.*	*a.*
0.103	3.762	0.0748	0.5428
0.103	3.682	0.0741	0.5368
0.104	4.045	0.0821	0.5317
0.104	4.089	0.0822	0.5375
0.104	4.255	0.0851	0.5396
0.104	4.274	0.0854	0.5402
0.104	4.316	0.0851	0.5474
0.103	3.197	0.0654	0.5276

Table XXVIII.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 50 Per Cent Methyl Alcohol and Water at 25°.

m.	*c.*	*v.*	*a.*
0.104	6.176	0.1104	0.6037
0.104	6.310	0.1128	0.6037
0.104	6.147	0.1114	0.5955

Table XXIX.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 50 Per Cent Methyl Alcohol and Water at 0°.

m.	*c.*	*v.*	*a.*
0.1048	2.8080	0.5730	0.5289
0.1048	3.1540	0.6410	0.5308
0.1048	3.1140	0.6340	0.5301

Table XXX.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 75 Per Cent Methyl Alcohol and Water at 25°.

m.	*c.*	*v.*	*a.*
0.104	6.058	0.1106	0.5912
0.104	4.534	0.0832	0.5881
0.104	4.474	0.0820	0.5888
0.107	1.903	0.0348	0.5902
0.107	2.954	0.0538	0.5926

Table XXXI.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 75 Per Cent Methyl Alcohol and Water at 0°.

m.	*c.*	*v.*	*a.*
0.099	3.092	0.0589	0.5666
0.099	3.021	0.0578	0.5641
0.099	3.055	0.0580	0.5686
0.096	3.000	0.0571	0.5670
0.098	3.033	0.0575	0.5693
0.095	1.680	0.0319	0.5685

In order to see the connection existing between the relative velocities of the anion of silver nitrate in water, methyl alcohol, and the various mixtures of these solvents, the following table is given :

Table XXXII.—Relative Velocity of the Anion of Silver Nitrate in Water, Methyl Alcohol, and Mixtures of these Solvents.

t.	0.	Twenty-five per cent.	Fifty per cent.	Seventy-five per cent.	One hundred per cent.
25°	0.5285	0.5538	0.6010	0.5902	0.5797
0°	0.5628	0.5379	0.5299	0.5673	0.5871

The values in this table are plotted in Fig. V., the abscissae representing the per cent of alcohol and the ordinates representing the relative velocity. The curve at 25°

shows a maximum value in the 50 per cent mixture, while at 0° a minimum value is shown in the same solvent. The curves are also exactly opposite in every respect. The course

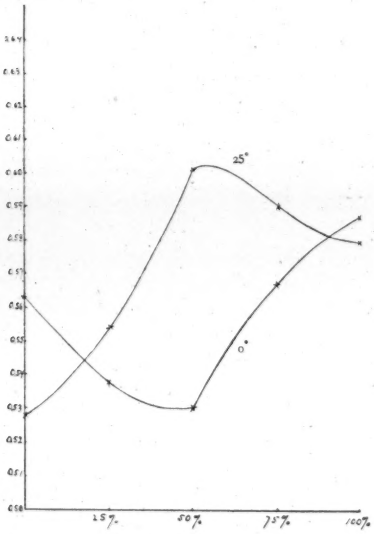


Fig. V.

of the curves may be explained as follows: The law of Kohlrausch[1] shows that the molecular conductivity at infinite dilution is equal to the sum of two independent constants, which are in fact the velocities of the ions at infinite dilution calculated in terms of conductivity units, that is,

$$A + C = \mu\infty,$$

A representing the anion, C the cation, and $\mu\infty$ conductivity at infinite dilution.

In this investigation, however, the conductivity at infinite

[1] Wied. Ann., **26**, 194 (1895).

dilution in these various solvents has not been determined, but by Ostwald's[1] modification of the law of Kohlrausch, which takes into account the amount of dissociation,

$$\alpha(A + C) = \mu\infty,$$

α representing the per cent of dissociation, it is possible to calculate αA and αC at any dilution if the ratio C/A is known. The ratio C/A has been determined for a N/10 solution of silver nitrate in these various solvents.

Hence, if we have the conductivities at 0° and at 25° of any dilution, we may calculate αC and αA, assuming that C/A is practically the same for dilutions of about the same order, which is not improbable. This has been done in the following table for a dilution of $v = 40$.

Table XXXIII.—Velocities of the Anion and Cation of Silver Nitrate in Water, Methyl Alcohol, and Mixtures of these Solvents Calculated in Conductivity Units.

	CH_3OH. 0 per cent.	CH_3OH. 25 per cent.	CH_3OH. 50 per cent.	CH_3OH. 75 per cent.	CH_3OH. 100 per cent.
Anion, 25°	58.25	40.24	34.65	30.88	30.96
" 0°	35.51	19.18	15.71	17.04	23.31
Cation, 25°	51.97	32.44	22.15	21.45	22.46
" 0°	27.59	16.46	12.92	12.99	16.40

Having calculated these values of C and A for the two temperatures, 0° and 25°, we may calculate the temperature coefficients of ionic mobility, not the true coefficients, however, but α (a constant) times the true coefficient. The variation of α, as was shown by Jones and Douglas,[2] is not appreciable over a range of 25°, and, therefore, the above procedure is allowable. This has been done in the following table.

A_{25} represents the ionic velocity of the anion at 25°, measured in conductivity units.

A_0 represents the ionic velocity of the anion at 0°, measured in conductivity units.

ΔA represents the difference in the velocities of the anion, between 0° and 25°, or is equal to $A_{25} - A_0$.

[1] Lehrbuch d. allg. Chem., II., 672.

[2] This JOURNAL, **26**, 428 (1901).

C_{25} represents the ionic velocity of the cation at 25°, measured in conductivity units.

C_0 represents the ionic velocity of the cation at 0°, measured in conductivity units.

C represents the difference in the velocities of the cation between 0° and 25°, or is equal to $C_{25} - C_0$.

φ_{25} represents fluidity of the solvent at 25°.

$\Delta\varphi$ represents the difference in the fluidity between 0° and 25°, or is equal to $\varphi_{25} - \varphi_0$.

Δt represents difference in temperature, or 25° — 0°.

φ_0 represents fluidity of the solvent at 0°.

Table XXXIV.—Comparison of the Relative Temperature Coefficients of Ionic Mobility for the Ions of Silver Nitrate in Water, Methyl Alcohol, and Various Mixtures of these Solvents, also the Temperature Coefficient of Mobility of Solvent.

	CH_3OH. 0 per cent.	CH_3OH. 25 per cent.	CH_3OH. 50 per cent.	CH_3OH. 75 per cent.	CH_3OH. 100 per cent.
$\frac{1}{A_{25}} \cdot \frac{\Delta A}{\Delta t}$	0.0156α	$0.0209\alpha_1$	$0.0230\alpha_2$	$0.0179\alpha_3$	$0.0098\alpha_4$
$\frac{1}{C_{25}} \cdot \frac{\Delta C}{\Delta t}$	0.0189α	$0.0197\alpha_1$	$0.0166\alpha_2$	$0.0153\alpha_3$	$0.0106\alpha_4$
$\frac{1}{\varphi} \cdot \frac{\Delta\varphi}{\Delta t}$	0.0249	0.0223	0.0216	0.0205	0.0121

The temperature coefficients of mobility of the solvents were calculated from the results of Traube,[1] Pagliani,[2] and Batelli.[3] The relative temperature coefficients for the anion and cation in the same solvent are strictly comparable, since α is a constant and therefore does not affect the result of the comparison.

From a consideration of these data it is seen that, in the pure solvents, water and methyl alcohol, the coefficient for the cation is greater, whereas in the mixture, that of the anion is greater. This being the case, C/A in the pure solvents would approach the limiting value 0.5, as the temperature rises, and

[1] Ber. d. chem. Ges., **19**, 871 (1889).
[2] Att. d. R. Ac. delle. Sc. d. Torrino.
[3] *Ibid.*

the beginning and end of the curve of relative velocities at 25° would be below the beginning and end of the curve for 0°.

Since in the mixtures the anion has a larger temperature coefficient, the curve for 25° will pass through a maximum, this maximum existing in that mixture where the irregularity between the two temperature coefficients is greatest, that is, the 50 per cent mixture.

If we know the value of α, the dissociation factor, we could calculate the true temperature coefficients from the relative coefficients.

At the dilution used ($v = 40$) the dissociation of silver nitrate in water is about 89 per cent, or $a = 0.89$. It has been shown by Jones and Carroll[1] in the case of certain salts, sodium iodide, potassium iodide, and potassium bromide, that in 50 per cent methyl alcohol $a = 0.91$ for $v = 32$, and 0.93 for $v = 64$. We should not make an appreciable error if we assume the value 0.91 for a in the case of silver nitrate in the 50 per cent mixture at $v = 40$. The real temperature coefficient would then be $0.0230 \times 0.91 = 0.0212$. Kohlrausch[2] has pointed out in the case of certain ions in aqueous solutions that the more nearly the temperature coefficients of ionic mobility and fluidity (of water) are equal, the greater is the effect of decrease in fluidity in lowering ionic mobility. This would probably be true for ions in mixed solvents.

Comparing, then, the temperature coefficients of mobility of anion and cation, and fluidity of the 50 per cent mixture, it is seen that the temperature coefficient of the $\overline{NO_3}$ ion (0.0212) is most nearly equal to that of fluidity (0.0216). Hence the effect of decrease in fluidity would be greatest in the case of the $\overline{NO_3}$ ion; that is, C/A would approach the limiting value 0.5, and, hence, the minimum in the curve in the 50 per cent mixture.

The fluidity is also decreased by change of composition, and the resulting change in ionic mobility will be greatest in the case of that ion whose temperature coefficient is most nearly

[1] This JOURNAL, 32, 521 (1904).
[2] Sitz. Ber. d. Berlin Ak., 1902, p. 572.

equal to the temperature coefficient of fluidity. This is the case with the $\overline{NO_3}$ ion; therefore, this ion will be the most affected, and the ratio between its velocity and that of the $\overset{+}{Ag}$ ion will become less, that is, approach the limit 0.5 and there will therefore be a minimum in the curve.

Conclusions.

1. A study of the conductivity of silver nitrate in water, methyl alcohol, and mixtures of these solvents, leads to the conclusion that silver nitrate is not an exception to the general phenomenon discovered by Zelinsky and Krapiwin[1] and studied extensively by Jones and Lindsay in this University. The minimum point in the conductivity was found for silver nitrate in these solvents at 25° as well as at 0°.

2. The conductivity of silver nitrate in water, ethyl alcohol, and mixtures of these solvents does not show a minimum point either at 25° or at 0°, but a study of the curves representing these conductivities leads to the conclusion that at 0° a minimum is approached.

3. By comparing the conductivities at 0° with those at 25° the conclusion can be drawn that the influence of one solvent on the other decreases with rise in temperature.

4. The difference in the relative velocities observed in the pure solvents at 0° and 25° become less as the temperature rises, and the velocities, therefore, tend toward equality. This has already been observed for pure solvents, but it does not hold in the case of mixed solvents. That exactly the opposite is true in most mixtures is seen by examining Fig. V.

5. The relative velocities are largely dependent on the nature of the solvent.

6. In mixed solvents the relative velocities are dependent on both the temperature and composition of the mixture.

[1] Ztschr. phys. Chem., 21, 35 (1897).

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE REACTIONS OF ETHYL CHLORSULPHONATE.

By O. W. Willcox.

Ethyl chlorsulphonate, $C_2H_5OSO_2Cl$, was first prepared by R. Williamson,[1] in 1857, and has since been studied by a number of chemists. The latest of these investigations was carried out in this laboratory by Bushong,[2] who studied its behavior towards sodium alcoholates and aniline and proved that it acts as an alkylating agent.

At the suggestion and under the supervision of Dr. J. U. Nef I have undertaken a further study of this interesting compound, with special reference to a complete and final explanation of all the reactions shown by it.

As is clearly evident from the work of Nef,[3] the alkylating properties of primary and secondary esters of sulphuric acid are due to the fact that the organic radicals in these compounds undergo a methylene dissociation. Ethyl sulphuric acid, for example, is partially dissociated at ordinary temperatures into ethylidene and sulphuric acid,

$$CH_3CH_2OSO_2OH \rightleftarrows CH_3CH = +H—OSO_2OH.$$

The well-known alkylating properties of the alkyl haloids, alkyl nitrates, sodium alcoholates, $C_nH_{2n+1}X$, $C_nH_{2n+1}ONO_2$, $C_nH_{2n+1}ONa$, are similarly due to the presence of dissociated methylene residues, $C_nH_{2n}=$, and the speed of the alkylation in the different cases must therefore be directly proportional to the percentage of such residues present at the reaction temperature—a fact which has been qualitatively verified by Nef's work, and which has also, in part, been demonstrated quantitatively by various observers.[4]

Since the work of Bushong obviously shows that ethyl chlorsulphonate is an alkylating agent, a dissociation of this substance into ethylidene and chlorsulphonic acid,

[1] J. Chem. Soc. (London), **10**, 97.

[2] This Journal, **30**, 212.

[3] Ann. Chem. (Liebig), **309**, 126–189; **318**, 1–57.

[4] Conrad: Ztschr. phys. Chem., **3**, 450; **4**, 631. Menschutkin: *Ibid.*, **5**, 589; **6**, 41. Burke and Donnan: J. Chem. Soc. (London), **85**, 555.

$$CH_3CH_2OSO_2Cl \rightleftarrows CH_2CH= + H—OSO_2Cl,$$

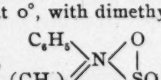
must exist and be capable of experimental demonstration. Whereas ethyl chloride does not dissociate completely into ethylene and hydrochloric acid until 550°, the dissociation-point of ethyl chlorsulphonate was found to be very low—namely, at 160°. Consequently the latter substance is, like diethyl sulphate, a far more energetic alkylating agent than chloride, bromide, or even iodide of ethyl.[1] It reacts, for instance, with ammonia in absolute ethereal solution with violence at 0°, giving a mixture of di-, tri-, and tetraalkylated ammonium chlorides. Under similar conditions a reaction with ethyl chloride and ammonia is hardly perceptible, and even with ethyl iodide proceeds only very slowly.

Incidentally, it was also demonstrated by experiment that chlorsulphonic acid—the other dissociation-product of ethyl chlorsulphonate—is partially dissociated further into sulphur trioxide and hydrogen chloride,

$$ClSO_2OH \rightleftarrows O_2S=O + H—Cl.$$

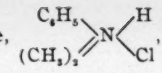
Since the products of dissociation of chlorsulphonic acid interact spontaneously on one another at 170°, or in the presence of catalytic agents even at 70°, with formation of equal molecules of sulphuryl chloride and sulphuric acid,[2]

$$2SO_3 + 2HCl \rightarrow SO_2Cl_2 + H_2SO_4,$$

it was impossible to determine the exact dissociating-point of chlorsulphonic acid, but it is undoubtedly low—not above 250°. Consequently, there must be a relatively large percentage of dissociated chlorsulphonic acid particles, SO_3 and HCl, present at ordinary temperatures in a preparation of chlorsulphonic acid. This was demonstrated in a most striking manner by treatment of this substance, in chloroform solution at 0°, with dimethylaniline, dimethylaniline sulphurtrioxide,  , and the hydrochloride of dimethyl-

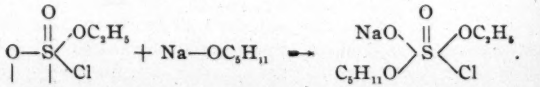
[1] Nef: Ann. Chem. (Liebig), **318**, 16, 40–50.

[2] Behrend: Ber. d. chem. Ges., **8**, 1004; Wold and Rüff: D. R. P., Kl. 17, 129,862. See Centrbl., 1902, I., 837.

aniline,  , being quantitatively formed.[1]

Chlorsulphonethyl ester, therefore, in its reactions with ammonia, amines, alcohols, phenols, and their salts, does not act as such, *i. e.*, in the molecular form, but by virtue of its being partially dissociated into ethylidene, $CH_3CH=$, sulphur trioxide, SO_3, and hydrogen chloride, HCl.

There are two series of reactions of ethyl chlorsulphonate which must, however, be explained on the basis of an action between the non-dissociated molecules, $ClSO_2OC_2H_5$, and the reagents used; namely, those with sodium alcoholates in absolute ethereal solution and those with sodium malonic ester and allied compounds. In the former case Bushong has observed the formation of addition-products, soluble in ether, which are decomposed by heat or by addition of water. The addition-product of ethyl chlorsulphonate and sodium isoamylate described by Bushong was isolated by me in large quantity and found, contrary to his statement, to be remarkably stable. It can be boiled for hours under a reflux condenser, in absolute ethereal solution, without change if rigid precautions are taken to prevent an access of moisture. The waxy mass left after distilling off the ether does not, in fact, decompose until heated to 200° at 30 mm. pressure. In view of all this, it is highly improbable that the addition-product possesses the constitution given to it by Bushong,



This is now, in fact, the only reaction of ethyl chlorsulphonate which requires further investigation. It is the intention of Dr. Nef to study this addition-product with great care with the object of determining its constitution rigidly.

Ethyl chlorsulphonate, in view of the results with amines, alcohols, and phenols, was expected to react with the sodium

[1] Cf. "Behavior of Formhydroxamic Acid towards Acetone." Biddle: Ann. Chem. (Liebig), 310, 14.

salts of acetoacetic ester, malonic ester, and allied compounds in a manner entirely analogous to ethyl halides, ethyl nitrate, and diethyl sulphate,[1] *i. e.*, to give α-ethylacetoacetic ether, ethylmalonic ester, etc. This is, however, not the case. The substance acts here as a chlorinating agent, giving, for instance, α-chloracetoacetic ester and chlormalonic ester. Sulphurous acid and alcohol are the other products formed.

This surprising and entirely unexpected result is due to the fact that the chlorine atom in the molecule of ethyl chlorsulphonate is unsaturated, and it therefore first absorbs the reagent,

$$(COOR)_2{=}CH{-}H + {=}Cl{-}SO_2OC_2H_5 \rightarrow (COOR)_2CH\diagdown\!\!\diagup Cl{-}SO_2OC_2H_5.$$
$$\qquad\qquad\qquad

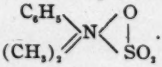
chlorinating agent, as well as the observation of Findeisen[1] that *p*-tolylsulphone chloride gives with sodium acetoacetic ester, *α*-chloracetoacetic ester, and sodium *p*-tolylsulphinate is naturally to be explained on an entirely analogous basis.

EXPERIMENTAL PART.

Preparation of Ethyl Chlorsulphonate.—The ethyl chlorsulphonate used in my work was prepared from sulphuryl chloride according to Bushong's modification of Behrend's method. It was found advisable to drop in the alcohol very slowly, to pass the current of air quite rapidly, and to dry the oil with anhydrous copper sulphate. By attending to these details the yield was raised to 80 per cent of the theory. Bushong states that the reaction-mixture separates into two layers, the lower consisting of ethyl chlorsulphonate. Although I have repeatedly prepared the substance in quantities of 200 grams, I have never been able to observe such a separation into layers.

Action of Chlorsulphonic Acid on Dimethylaniline.

The action of chlorsulphonic acid on dimethylaniline has such a significance for the chemistry of ethyl chlorsulphonate in its action with ammonia and amines that it is presented at this point.

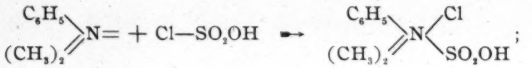
Twenty-three grams of dimethylaniline, diluted with 80 cc. of chloroform, were placed in a quarter-liter flask and cooled by means of ice and salt. 19.5 grams of chlorsulphonic acid (0.5 molecule) were then slowly added by means of a dropping-funnel, the flask being constantly shaken. A granular precipitate appeared after the addition of the first few drops, and the interaction took place almost instantly. The precipitate was filtered, and washed with cold chloroform until it gave no test for chlorine ions. When freed from adhering chloroform on a porous plate, over sulphuric acid, in a vacuum, the precipitate consists of practically pure dimethylanilinesulphurtrioxide,  . The other reaction-prod-

[1] J. prakt. Chem., [2], 68, 529.

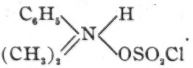
uct, phenyldimethylammonium chloride, is very soluble in chloroform and consequently is found, together with small quantities of dimethylaniline sulphurtrioxide, in the chloroform filtrate.

The formation of these products, as discussed in the introduction, is self-evident on the basis of a partial dissociation of the chlorsulphonic acid molecules into sulphur trioxide and hydrogen chloride. The dissociated portions are then simply very rapidly absorbed by the excess of dimethylaniline molecules present.

Two other possible interpretations of the reaction have been carefully considered: I., the formation of an addition-product,



and II., of a salt-like compound,



Either of these hypothetical intermediate products must then be supposed to lose hydrogen chloride almost instantly at —15° and give the products actually obtained in the reaction under discussion. These interpretations, however, have not such inherent probability as the one adopted above. Williams'[1] vapor-density determinations of chlorsulphonic acid, at temperatures above 180°, show that the substance is partially dissociated into sulphur trioxide and hydrogen chloride. The vapor density of sulphuric acid at 400° proves that it is dissociated completely into sulphur trioxide and water at that temperature, and at 332° 34 per cent of the molecules of this acid are thus dissociated.[2] It is therefore self-evident that even at —15°, or at much lower temperatures, some molecules of chlorsulphonic acid are dissociated, equilibrium being maintained in the sense of the equation,

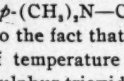
[1] J. Chem. Soc. (London), [2], **7**, 304.
[2] Deville and Troost: Compt. rend., **56**, 891.

$$ClSO_2OH \rightleftarrows SO_3 + HCl;$$

addition of dimethylaniline must at once destroy this equilibrium and cause the reaction from left to right to proceed to completion.

According to Evans[1] the action of chlorsulphonic acid on dimethylaniline results in the formation of dimethylaniline-*p*-sulphonic acid, $p\text{-}(CH_3)_2N—C_6H_4SO_2OH$. This result is undoubtedly due to the fact that Evans took no precautions to prevent a rise of temperature on mixing his reagents. Dimethylaniline sulphur trioxide, which is the primary reaction-product, undergoes, on being heated to about 60°, a spontaneous transformation into the isomeric *p*-dimethylaniline-*p*-sulphonate (by intramolecular addition, see below).

Ethyl Chlorsulphonate and Dimethylaniline.

Dimethylanilinesulphurtrioxide,  .—The action of ethyl chlorsulphonate on dimethylaniline has already been studied by Wenghöffer,[2] who obtained dimethylaniline-*p*-sulphonic acid and ethyl chloride as reaction-products,

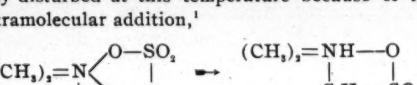
$$C_6H_5N(CH_3)_2 + ClSO_2OC_2H_5 \rightarrow p\text{-}(CH_3)_2NC_6H_4—SO_2OH + C_2H_5Cl.$$

He obviously took no precautions to control the temperature on mixing his reagents, and consequently the intermediate formation of dimethylanilinesulphurtrioxide escaped his notice; furthermore, a large amount (20 per cent) of phenyldimethylethylammonium chloride is also formed in this reaction.

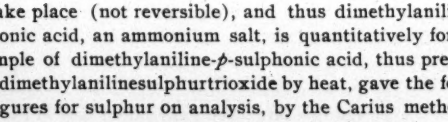
Fifty grams of dimethylaniline (2 molecules), diluted with an equal volume of chloroform, were thoroughly cooled by means of salt and ice; 30 grams of ethyl chlorsulphonate, similarly diluted, were then slowly added by means of a dropping-funnel, care being taken to shake vigorously during this operation. The reaction is practically completed as soon as

[1] Chem. News, 73, 53.
[2] J. prakt. Chem., [2], 16, 448.

all the ethyl chlorsulphonate has been added, and the white, granular precipitate of dimethylanilinesulphurtrioxide is filtered off, washed with chloroform, and dried on a clay plate. A very careful comparison with the precipitate obtained by treating dimethylaniline with chlorsulphonic acid, as described above, showed that the products are identical. Dimethylanilinesulphurtrioxide is somewhat soluble in chloroform, hence the yield is not quantitative; 34.5 grams of the product were obtained, which is 83.3 per cent of the theory. When dimethylanilinesulphurtrioxide is heated to about 60° it is transformed quantitatively into dimethylaniline-*p*-sulphonic acid: the equilibrium between the active and inactive dimethylanilinesulphurtrioxide particles (see below),



is finally disturbed at this temperature because of the fact that intramolecular addition,[1]



can take place (not reversible), and thus dimethylaniline-*p*-sulphonic acid, an ammonium salt, is quantitatively formed. A sample of dimethylaniline-*p*-sulphonic acid, thus prepared from dimethylanilinesulphurtrioxide by heat, gave the following figures for sulphur on analysis, by the Carius method:

0.3493 gram substance gave 0.3953 gram $BaSO_4$.

	Calculated for $(CH_3)_2NH{-}C_6H_4{-}O{-}SO_3$	Found.
S	15.92	15.65

The sodium salt of this acid was also prepared and compared with the corresponding salt, made according to the directions in the literature.

The chloroform filtrate from the 34.5 grams dimethylani-

[1] Nef: Ann. Chem. (Liebig), **318**, 33-35; cf. *Ibid.*, **298**, 223-225.

linesulphurtrioxide was now worked up. Careful fractionation gave 9.9 grams of ethyl chloride (b. p. 12°), or 80 per cent of the theory. Further distillation, finally at reduced pressure, gave 19.7 grams unchanged dimethylaniline. The pasty residue now remaining in the distilling-flask consisted of ethyldimethylphenylammonium chloride and the dimethylaniline salt of dimethylaniline-*p*-sulphonic acid, which naturally must be formed by the action of heat on the dimethylanilinesulphurtrioxide which was dissolved in the chloroform.

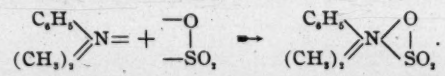
The tetraalkylated ammonium salt was obtained from this mixture by adding strong aqueous caustic soda, extracting the dimethylaniline thus set free by ether, and then neutralizing the aqueous solution with hydrochloric acid, and evaporating to dryness. The residue was then extracted with alcohol, and thus 7 grams of ethyl dimethylphenylammonium chloride were obtained. The chlorplatinate, which crystallizes from 80 per cent alcohol in beautiful yellow needles, was prepared and analyzed:

0.5059 gram substance gave 0.1408 gram Pt.

0.5980 gram substance gave 24 cc. N_2 at 20° and 750 mm. pressure.

	Calculated for $\left[\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!N(CH_3)_2\right]_2PtCl_4$.	Found.
Pt	27.33	27.83
N	3.96	4.26

The results obtained in this experiment are in harmony with the conclusion that ethyl chlorsulphonate contains the following dissociated particles: I., ethylidene, $CH_3CH=$; II., sulphurtrioxide, SO_3; and III., hydrogen chloride, HCl. The sulphur trioxide combines with the dimethylaniline to give dimethylanilinesulphurtrioxide,



The hydrogen chloride is in part, 80 per cent, absorbed by

the ethylidene, thus giving ethyl chloride, and is also in part, 20 per cent, taken up by the dimethylaniline present in excess, thus forming phenyldimethyl ammonium chloride. The latter substance is then immediately converted by the remainder of the available alkylidene into ethyldimethylphenylammonium chloride.[1]

Special experiments have shown, furthermore, that dimethylanilinesulphurtrioxide can also be prepared by cautious addition of sulphur trioxide to a well cooled solution of dimethylaniline in chloroform. The analogous compound, triethylaminesulphurtrioxide, $(C_2H_5)_3{\equiv}N\langle^{O}_{SO_2}$, has in fact long been known, having been prepared by Beilstein and Wiegand[2] by mixing the two components in molecular proportions.

An interpretation of the reaction between dimethylaniline and ethyl chlorsulphonate on the basis of an intermediate formation of the addition-product,

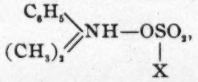
$$\begin{matrix} C_6H_5 \\ (CH_3)_2 \end{matrix}\!\!>\!N\!<\!\begin{matrix} Cl \\ SO_2OC_2H_5 \end{matrix},$$

which must then immediately break down at $-15°$ into ethyl chloride and dimethylanilinesulphurtrioxide has also been carefully considered; it is *à priori* highly improbable in view of the properties of ethyl chlorsulphonate and chlorsulphonic acid. Furthermore, it is impossible to explain on this basis the fact that 20 per cent of ethyl dimethylphenylammonium chloride is formed in this reaction, since ethyl chloride and dimethylaniline do not combine under the conditions employed. Finally, this interpretation of the reaction is also excluded by the data obtained in the study of the reaction

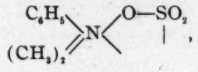
[1] Nef: Ann. Chem. (Liebig), 309, 162-163.
[2] Ber. d. chem. Ges., 16, 1264.

between ethyl chlorsulphonate and ammonia as well as diethylamine (see below).[1]

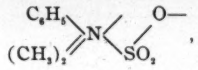
Properties of Dimethylanilinesulphurtrioxide. — Dimethylanilinesulphurtrioxide shows the properties of an unsaturated compound to a marked extent, absorbing water, alcohol, phenol, ammonia, primary and secondary amines, olefines, and acetone with great ease. In view of the fact that the resulting addition-products possess the general formula,



it must be concluded that the original compound possesses relatively the larger percentage of active A-molecules,



as compared with active B-molecules,



for instance.

[1] The reaction taking place between tertiary amines and acyl chlorides, including chlorcyanogen, whereby acylated dialkylamines and alkyl chlorides,

$$R_3N + Cl{-}A \longrightarrow R_2N{-}A + RCl,$$

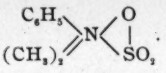
are formed [cf. Staedel: Ber. d. chem. Ges., **19**, 1947; Braun: *Ibid.*, **35**, 1279], have been interpreted in the literature from the standpoint of an intermediate formation of the addition-product, $R_3N\langle^{Cl}_{A}$.

There is, however, in view of my work [cf. Ann. Chem. (Liebig), **308**, 227, 269; **309**, 160–165; **318**, 182], another possible, and, as it seems to me, far more probable explanation of these reactions. A trisubstituted ammonia is partially dissociated at ordinary temperature into alkylidene and a secondary amine,

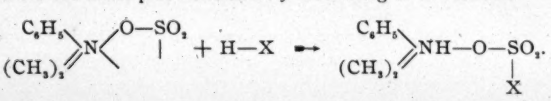
$$(C_nH_{2n+1})_3{\equiv}N \rightleftarrows C_nH_{2n}{=} + (C_nH_{2n+1})_2NH.$$

An analogous dissociation exists in the case of primary and secondary amines, but these need not be considered here. This explains why triethylamine gives acetaldehyde in the cold with aqueous permanganate [Claisen, Wallach: Ber. d. chem. Ges., **8**, 1239], and why Hofmann's reaction, as is well known, is reversible. In the reactions referred to, the acyl chloride therefore probably acts first with the dissociated tertiary amine particles, *i. e.*, with the secondary amine, to give the acylated secondary amine, and the hydrogen chloride thus formed is at once taken up by the alkylidene with formation of alkyl chloride. It is my intention to investigate these reactions in the near future with the object of testing experimentally the correctness of the views here presented. J. U. Nef.

These are naturally in equilibrium with the inactive molecules,



The addition of a reagent to dimethylanilinesulphurtrioxide therefore takes place exclusively[1] according to the scheme



The molecular rearrangement of the substance at 60° to dimethylaniline-*p*-sulphonic acid, mentioned above, is therefore also simply due to an intramolecular addition of the active A-molecules of dimethylanilinesulphurtrioxide.

Dimethylanilinesulphurtrioxide and Water.—Dimethylanilinesulphurtrioxide is very quickly acted upon by hot, but not so readily by cold, water; once moistened with water it is, however, impossible to prevent an action from setting in sooner or later. Freshly prepared dimethylanilinesulphurtrioxide can be washed with ice-water, spread out on a clay plate, and kept for some hours without apparent change. Eventually a spot of liquefaction will appear in the mass. Other spots then quickly appear and grow rapidly until, in a few seconds, the whole mass is transformed, with marked rise of temperature, into a liquid which, on cooling, solidifies to a mass of white crystals. The same phenomena are observed, after some time, when water and dimethylanilinesulphurtrioxide are brought together in molecular proportions at ordinary temperatures. The resulting crystalline product, when treated with aqueous sodium hydrate, gives, quantitatively, sodium sulphate and dimethylaniline. This fact, as well as the synthesis from equimolecular quantities of water and dimethylanilinesulphurtrioxide, identifies the addition-product as primary dimethylphenylammonium sulphate, $C_6H_9(CH_3)_2NHOSO_2OH$. The salt is very soluble in

[1] Cf. Nef: Ann. Chem. (Liebig), **298**, 204: **318**, 31; **335**, 198–199.

water and alcohol, and melts at 84° to 85°. Heated to 200° it is transformed, with loss of water, into dimethylaniline-*p*-sulphonic acid.

0.7214 gram substance gave 0.7890 gram $BaSO_4$.

	Calculated for $(CH_3)_2NH(C_6H_5)OSO_2OH$.	Found.
S	14.64	15.01

Dimethylanilinesulphurtrioxide and Alcohol.—Equimolecular quantities of dimethylanilinesulphurtrioxide and absolute alcohol unite, with marked evolution of heat, to give dimethylphenylammonium ethyl sulphate,

$$C_6H_5(CH_3)_2NHOSO_2OC_2H_5.$$

The salt solidifies, on cooling, to globular masses of radiating needles, melting at 54°. It is quite soluble in water and alcohol, and decomposes when heated to 200° with considerable charring. Treated with aqueous potassium hydrate, it gives dimethylaniline and potassium ethyl sulphate, thus establishing its constitution.

Dimethylanilinesulphurtrioxide and Acetone.—When dimethylanilinesulphurtrioxide is warmed gently with an excess of acetone the solid disappears, and there is a separation into two layers. The lower layer, on cooling, solidifies to a mass of large prismatic crystals, melting at 76° to 78°. The addition-product is soluble in water, but is decomposed both by acids and alkalies, giving acetone, sulphuric acid, and dimethylaniline.

1.1089 grams substance gave 1.000 gram $BaSO_4$.

	Calculated for $C_{11}H_{17}O_4NS$.	Found.
S	12.35	12.38

Two formulas are possible for this substance:

I. $(CH_3)_2(C_6H_5)NH—O—SO_2—O—C\begin{matrix}CH_2\\ \\ CH_3\end{matrix}$;

and

II. $(CH_3)_2(C_6H_4)N\begin{matrix}O\\ \\ SO_2\end{matrix}>C=(CH_3)_2$.

An addition-product is also obtained by dissolving dimethylanilinesulphurtrioxide in warm malonic ester. On cooling, white leaflets are obtained which give, on treatment with aqueous alkali, malonic ester, sulphuric acid, and dimethylaniline.

Dimethylanilinesulphurtrioxide and Phenol.—When these two substances are brought together in molecular proportions they unite, with evolution of heat, to give dimethylphenylammoniumphenylsulphate, $C_6H_5(CH_3)_2NHOSO_2OC_6H_5$. This salt was obtained in the crystalline form. It is very soluble in water and is decomposed by aqueous potassium hydroxide, quantitatively, into dimethylaniline and potassium phenylsulphate. Consequently this is probably the easiest way to prepare the latter substance. An analysis of the potassium phenylsulphate obtained gave the following result:

0.4067 gram substance gave 0.1609 gram K_2SO_4.

	Calculated for $C_6H_5OSO_2OK$.	Found.
K	18.39	17.73

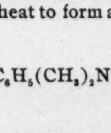
The salt obtained was also compared very carefully with a preparation made according to the method of Baumann.[1]

Dimethylanilinesulphurtrioxide and Aniline.—These two substances unite very energetically when brought together in molecular proportions. A wax-like salt is formed which is decomposed by baryta water into dimethylaniline and barium phenylsulphamate, thus establishing the constitution as

$$C_6H_5(CH_3)_2NHOSO_2—NH.C_6H_5.$$

The sulphamate was identified by its reactions, and by comparison with the corresponding product obtained from aniline and ethyl chlorsulphonate (see below).

Dimethylanilinesulphurtrioxide and Trimethylethylene.—*β*-Isoamylene and dimethylanilinesulphurtrioxide unite with slight evolution of heat to form an indistinctly crystallized substance, obviously



.—It is decom-

[1] Ber. d. chem. Ges., 11, 1907.

posed by water into dimethylaniline, sulphuric acid, and amylene.

The results here presented[1] suffice to show very clearly that dimethylanilinesulphurtrioxide is an excellent carrier of sulphur trioxide. They indicate an excellent means of preparing the monoalkylated sulphuric and sulphamic acids.

Ethyl Chlorsulphonate and Diethylamine.—Thirty-nine grams of diethylamine, diluted with 200 cc. absolute ether, were placed in a flask surrounded by ice and salt; 38 grams of ethyl chlorsulphonate (0.5 molecule), diluted with twice its volume of absolute ether, were added through a dropping-funnel. A white precipitate appeared at once and the odor of sulphonate was soon gone. Water was added until the precipitated salts had dissolved. The ether was separated from the aqueous layer, dehydrated with calcium chloride, and then distilled off on a water-bath. A small amount, 4 grams, of oily liquid remained, and this, on heating under reduced pressure to remove the last traces of ether, soon solidified. On crystallization from benzene colorless, orthorhombic prisms, melting at 89°, were obtained, which dissolve in water with a strongly acid reaction. The analysis and properties[2] prove that it is free diethylaminsulphonic acid,

$$(C_2H_5)_2N{-}SO_2OH.$$

0.3463 gram substance gave 29.8 cc. N_2 at 20° and 754 mm. pressure.

[1] The interaction between sulphuric acid and alcohols, as well as ammonia and primary and secondary amines, which results, as has long been known, in the formation of primary alkyl sulphates and derivatives of aminosulphonic acid, respectively, $C_nH_{2n+1}.OSO_2OH$ and NH_2SO_2OH, must, in the light of the data here presented, be interpreted as follows: The alcohol, H—OR, or the amine, H—NR_2, is absorbed by the active sulphur trioxide molecules, O—SO_2, present at ordinary temperatures in sulphuric acid,

$$H_2SO_4 \rightleftarrows SO_3 + H_2O.$$

This explains why ether, which contains only a very small percentage of ethylidene particles at ordinary temperatures, but nevertheless decidedly more than ethyl alcohol, reacts only very slowly with concentrated sulphuric acid, in the cold, to give monoethylsulphuric acid. Ethyl alcohol, on the other hand, reacts at once, and with marked evolution of heat, with H_2SO_4, at ordinary temperatures, to form primary ethyl sulphate because it can add itself to the sulphur trioxide molecules present in the solution, whereas this is impossible in the case of ether. J. U. Nef.

[2] Behrend: Ann. Chem. (Liebig), **222**, 116.

0.4744 gram substance gave 0.7148 gram $BaSO_4$ (Carius).

	Calculated for $(C_2H_5)_2NSO_3OH$.	Found.
S	20.21	20.68
N	9.20	9.76

The aqueous solution, containing the main reaction-products, was now treated in a flask with an excess, 70 grams, of barium hydroxide, and finally heated in an oil-bath until the water, etc., had practically all distilled over. The distillate gave, on addition of solid caustic potash, and subsequent fractionation, 20 grams of basic oil boiling from 60° to 90°, and was, therefore, obviously a mixture of di- and triethylated ammonia. This oil, after thorough drying over solid potassium hydroxide, was diluted with an equal volume of absolute alcohol. Fifty grams of diethyl oxalate were added, and the mixture was then heated in a sealed tube, for four days, in a Kekulé water-bath.[1] The tube contents, on distillation, now gave 10 grams of triethylamine boiling at 90°. The chlorplatinate was prepared and analyzed:

0.2373 gram substance gave 0.0759 gram Pt.

	Calculated for $[(C_2H_5)_2NH]_2PtCl_4$.	Found.
Pt	31.89	31.87

The salt residue left in the flask after treatment with barium hydroxide and removal of volatile bases and water, was now powdered and treated with water and carbon dioxide, to get rid of the excess of barium hydroxide. The solution was then filtered, and evaporated to dryness on a water-bath. The residue, after further drying over sulphuric acid in a vacuum, was placed in a Soxhlet apparatus and extracted thoroughly with chloroform. The chloroform solution was found to contain 5 grams of an extremely deliquescent salt which answered in all respects to the properties of tetraethylammonium chloride. The chlorplatinate gave the following analytical data:

0.1498 gram substance gave 0.0443 gram Pt.

	Calculated for $[(C_2H_5)_4N]_2PtCl_4$.	Found.
Pt	29.23	29.55

[1] Method of Duvillier and Buisine: Ann. chim. phys., [5], 23, 289.

The residue left in the Soxhlet apparatus, undissolved by chloroform, was now digested for one hour with alcohol, whereupon only barium chloride remained undissolved. The alcoholic extract contained 30 grams of barium diethylsulphamate with some barium chloride. The latter was removed by dissolving the mixture in water, digesting with silver oxide, and subsequently treating with carbon dioxide, filtering, and evaporating to dryness. The barium salt is finally obtained in white needles.

0.8311 gram substance gave 0.4258 gram $BaSO_4$.

0.5644 gram substance gave 0.9572 gram $BaSO_4$ (Carius).

0.9923 gram substance gave 21.1 cc. N_2 at 22° and 756 mm. pressure.

	Calculated for $[(C_2H_5)_2NSO_2O]_2Ba.2H_2O$.	Found.
Ba	28.78	28.44
S	13.40	13.55
N	5.86	6.06

The products formed in the action of ethyl chlorsulphonate on diethylamine are, therefore, diethylaminosulphonic acid and tri- and tetraethylated ammonium chlorides—*i. e.*, the diethylamine is both alkylated and sulphonated. In view of the facts presented in this paper this reaction must be interpreted as follows :

I. $ClSO_2OC_2H_5 \rightleftarrows$

$$ClH + O{-}SO_2 + CH_3CH{=} + 2(C_2H_5)_2NH \rightarrow$$

$$CH_3CH_2N(C_2H_5)_2.HCl + HO{-}SO_2{-}N(C_2H_5)_2;$$

II. $(C_2H_5)_3N\langle^{H}_{Cl} + {=}CH{-}CH_3 \rightarrow (C_2H_5)_4NCl.$

Diethylsulphamic Acid Ethyl Ester, $(C_2H_5)_2NSO_2OC_2H_5$.—It was first of all important to prove rigidly, by experiment, that diethylaminosulphone ethyl ester is not the intermediate product formed in the reaction between diethylamine and ethyl chlorsulphonate. This substance might be formed by the metathetical reaction,

$$(C_2H_5)_2NH + ClSO_2OC_2H_5 \rightarrow (C_2H_5)_2NSO_2OC_2H_5 + HCl,$$

or through an intermediate formation of an addition-product, according to the equation,

$$(C_2H_5)_2NH= + Cl{-}SO_2OC_2H_5 \rightarrow (C_2H_5)_2NH\begin{matrix}Cl\\ SO_2OC_2H_5\end{matrix},$$

by subsequent loss of hydrogen chloride.

In view of the experiments of Nef with the alkylated sulphates, there was a strong possibility that diethylaminosulphone ethyl ester, $(C_2H_5)_2NSO_2OH + =CHCH_3$, provided it possesses a low point of dissociation, might in reality be the active alkylating agent in the reaction under consideration.

The same remarks hold good in the case of the interaction between ethyl chlorsulphonate and ammonia or aniline, *i. e.*, there is a possibility that aminosulphone ethyl ester or phenylaminosulphone ethyl ester, respectively,

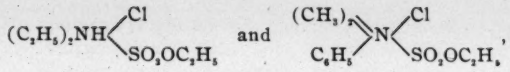
$$NH_2{-}SO_2OC_2H_5 \quad \text{or} \quad C_6H_5NHSO_2OC_2H_5,$$

may really be the active alkylating agents in these instances.

This possibility was, however, rigidly excluded in the case of diethylamine by actually synthesizing diethylsulphamic ethyl ester. It is not an alkylating agent at ordinary temperatures (see below), nor does it give ethyl chloride by treatment in the cold with an excess of dry hydrogen chloride. Since it is, moreover, highly probable that by the latter treatment some molecules of

$$(C_2H_5)_2{=}N{-}SO_3OC_2H_5$$
$$\begin{matrix}H & Cl\end{matrix}$$

must be formed, one must conclude that a substance of this character does not dissociate spontaneously into ethyl chloride and diethylsulphamic acid—an assumption which would have to be made in case the reactions of ethyl chlorsulphonate with di- and trialkylated amines were interpreted from the standpoint of an intermediate formation of the addition-products,



respectively. Finally, such an interpretation of these reactions is absolutely excluded in both cases because mixtures of a di- or a trialkylated amine and ethyl chloride do not interact perceptibly on one another at 0°.[1] The reactions of ethyl chlorsulphonate with ammonia, primary, secondary, and tertiary amines must, therefore, take place in the manner suggested above.

Diethylaminosulphone chloride, made according to the directions of Behrend,[2] was dissolved in absolute alcohol and treated with the theoretical amount of sodium ethylate; sodium chloride was deposited slowly. After two hours' standing the mixture was poured into water, and the oil which separated out was taken up in ether and dried with calcium chloride. The oil remaining, after distilling off the ether, had a yellow color and a disagreeable odor. On fractionating twice at reduced pressure diethylaminosulphone ethyl ester is obtained as a colorless, pleasant smelling oil boiling at 119° at 15 mm., and at 126° at 22 mm. pressure. Heated under atmospheric pressure, it decomposes with much charring.

0.3718 gram substance gave 0.4893 gram $BaSO_4$ (Carius).

0.3041 gram substance gave 19.8 cc. N_2 at 18° and 747 mm. pressure.

	Calculated for $C_4H_{11}O_2NS$.	Found.
S	17.67	18.00
N	7.73	7.40

Diethylsulphamic ethyl ester and diethylamine do not interact at ordinary temperatures when mixed in absolute ether solution. Dry ammonia is also without action under the same conditions. Consequently the substance does not act as an alkylating agent at 20° with ammonia or diethylamine; it cannot, therefore, be an intermediate product in the interac-

[1] Cf. Menschutkin: Ztschr. phys. Chem., **5**, 589.

[2] Ann. Chem. (Liebig), **222**, 116.

tion between diethylamine and ethyl chlorsulphonate. The ester is, furthermore, recovered entirely unchanged when an ethereal solution has been saturated with dry hydrogen chloride. It was also not appreciably affected after twenty-four hours' standing with concentrated aqueous hydrochloric acid, in which it is insoluble. This indicates, therefore, that the substance is an exceedingly weak base or is entirely devoid of basic properties.

Ethyl Chlorsulphonate and Ammonia.—The action of ethyl chlorsulphonate on ammonia has been studied by Baumstarck[1] and by Purgold,[2] but no decisive results were obtained. These reagents act with great violence on one another. The reaction must therefore be carried out in ether or benzene solution. The ethyl chlorsulphonate, diluted with ten times its volume of dry solvent, was cooled by means of ice and salt, and dry ammonia led in until the odor of the ester had disappeared. The main reaction-products are found in the deliquescent precipitate, which is filtered off and kept in a desiccator. The filtrate contained a small amount of material, the character of which varied with each experiment. In one case, using ether as a solvent, 2 cc. of triethylamine, boiling from 88° to 90°, were obtained. In another experiment, using the same solvent, 2 grams of a neutral, sweet-smelling oil containing nitrogen and sulphur were obtained. This gave, by hydrolysis with barium oxide, a barium salt soluble in water but insoluble in alcohol. Since the salt differed from barium diethylsulphamate, which is soluble in alcohol, and also was not identical with barium sulphamate, it was probably barium ethylsulphamate, and therefore the original oil must have been ethylaminosulphone ethyl ester. In a third experiment with ammonia and ethyl chlosulphonate, using benzene as a solvent, 3 grams of diethylaminosulphone ethyl ester, boiling at 117° to 119° at 15 mm. pressure, were obtained, identical in properties with the synthetic product described above. A nitrogen determination gave the following result:

[1] Ztschr. für Chemie, 1867, p. 567.
[2] Ber. d. chem. Ges., 6, 502.

0.2310 gram substance gave 14.9 cc. N_2 at 18° and 751 mm. pressure.

	Calculated for $C_8H_{15}O_2NS$.	Found.
N	7.74	7.42

As mentioned above, the main reaction-products (95 per cent) are insoluble in benzene or ether. One hundred grams of the dry precipitate were first extracted in a Soxhlet tube with chloroform; 18 grams of brown, syrupy salts were obtained, consisting of a mixture of di-, tri-, and tetraethylated ammonium chlorides. These were separated by digesting with an excess of aqueous barium hydroxide and subsequent distillation. The aqueous distillate gave, with caustic potash, etc., 6 grams of basic oil, boiling from 60° to 90°. It contained about equal parts of diethyl- and triethylamine, as determined by treatment with ethyl oxalate (see above). No ethylamine was found as a reaction-product. The residue left in the flask after water and volatile bases had been expelled gave, on extraction with chloroform, 7 grams of tetraethylammonium chloride. The chlorplatinate gave the following result on analysis:

0.2136 gram substance gave 0.0624 gram Pt.

	Calculated for $[(C_2H_5)_4N]_2PtCl_6$.	Found.
Pt	29.33	29.21

The original precipitate left in the Soxhlet apparatus, undissolved by chloroform, contains nothing which is soluble in alcohol. It dissolves in water with strongly acid reaction and gives a copious test for sulphate. The amount of sulphur removable from the precipitate as barium sulphate was determined quantitatively to be 11 per cent, whereas the total sulphur content by the Carius method was found to be 22 per cent. It is highly probable, from what follows, that the precipitate consists chiefly of ammonium chloride and ammonium imidosulphonate, $NH[SO_2ONH_4]_2$. The latter, on treatment with water, is split into equal molecules of sulphuric and aminosulphonic acids. The precipitate was first digested with an excess of aqueous barium hydroxide to ex-

pel the ammonia; carbon dioxide was then passed into the solution to get rid of excess of barium hydroxide. The filtrate now contained only barium chloride and barium sulphamate. The amount of chlorine in the solution was determined by titration, whereupon the calculated amount of silver sulphate was added in order to remove barium chloride. The filtrate, after treatment with carbon dioxide and hydrogen sulphide, was evaporated to dryness. The residue gave, on crystallization from dilute alcohol, 33 grams of pure barium sulphamate.

0.4784 gram substance gave 0.3121 gram $BaSO_4$.

	Calculated for $Ba(SO_2NH_2)_2$.	Found.
Ba	38.28	38.15

Treated with nitrous acid, in aqueous solution, the salt gives nitrogen and barium sulphate. Heated on a platinum foil, it gives white fumes, leaving a residue of barium sulphate.

The mechanism of the reaction between ammonia and ethyl chlorsulphonate is obviously analogous to the one taking place between this reagent and diethylamine. The ammonia is absorbed by the ethylidene, giving substituted ammonias, and these promptly take up hydrogen chloride to form salts which may also subsequently be further alkylated. Two molecules of sulphur trioxide must react with 1 molecule of ammonia to give imidosulphonic acid,

$$H{-}NH{-}H + 2O{-}SO_2 \rightarrow$$

$$HOSO_2{-}NH{-}H + O{-}SO_2 \rightarrow$$

$$HOSO_2{-}NH{-}SO_2OH,$$

which is then mainly converted into the ammonium salt.

Raschig[1] has shown that imidosulphonic acid is readily split by water into equal molecules of sulphuric and sulphamic acid, and this explains why imidosulphonic acid was not obtained, as such, in the experiments above described.

The fact that mono- and diethylated sulphamic ethyl

[1] Ann. Chem. (Liebig), 241, 178; cf. also Berglund: Ber. d. chem. Ges., 9, 1896.

esters, $C_2H_5NHSO_2OC_2H_5$ and $(C_2H_5)_2NSO_2OC_2H_5$, are occasionally formed in small quantities as reaction-products indicates the energetic alkylating properties of ethyl chlorsulphonate under the given conditions.

Ethyl Chlorsulphonate and Aniline.—The action of aniline on ethyl chlorsulphonate has been studied by Wenghöffer[1] and by Bushong.[2] The former obtained only sulphanilic acid and ethyl chloride as reaction-products. Shortly after the publication of Wenghöffer's paper, a preliminary notice by Wagner[3] appeared in which he stated that the formation of phenylsulphamic acid had been overlooked by Wenghöffer. Bushong observed the formation of ethylaniline in this reaction, and, citing the work of Wagner and Bamberger,[4] surmized that phenylsulphamic acid must also have been formed, but he apparently made no attempt to isolate the product.

In investigating this reaction I have found that when ethyl chlorsulphonate is added to aniline, without any attempt to control the decided evolution of heat, much ethyl chloride, as well as sulphanilic acid is formed; if, however, the aniline is cooled by means of ice and salt not a trace of these products is obtained.

Eighty grams of aniline, diluted with absolute ether and well cooled, were treated with 62 grams of ethyl chlorsulphonate (0.5 molecule), also diluted with pure ether. The reaction-products were found exclusively in the precipitate which was filtered off and dissolved in water. The aqueous solution, as in the corresponding case with ammonia, was found to give a strongly acid reaction and to contain much sulphate. This latter is, undoubtedly, due to the hydrolysis of phenylimidodisulphonic acid, which must be split by water into equal molecules of sulphuric and phenylsulphamic acids.

The aqueous solution was therefore first digested with an excess of barium hydroxide, and the volatile bases carried over with steam and extracted by ether. Forty-seven grams of oil, boiling from 180° to 204°, were thus obtained. It con-

[1] J. prakt. Chem., [2], **31**, 1803.
[2] This JOURNAL, **30**, 223.
[3] Ber. d. chem. Ges., **19**, 1157.
[4] *Ibid.*, **30**, 2275.

sisted chiefly of a mixture of about equal parts of aniline and monoethylaniline. The oil gave, on treatment with nitrous acid in dilute aqueous hydrochloric acid solution, 24 grams of ethyl phenylnitrosamine.

The solution from which the volatile bases had been removed was now worked up for barium phenylsulphamate in the following manner: It was first filtered from much barium sulphate, treated with carbon dioxide to get rid of excess of barium hydroxide, and then evaporated on a water-bath to incipient crystallization, taking care to add ammonia occasionally in order to keep the solution alkaline.[1] After recrystallizing twice from dilute ammonia water, 28 grams of pure barium phenylsulphamate were obtained, showing the following properties: It is hydrolyzed readily by boiling with dilute hydrochloric acid; on treatment with nitrous acid, barium sulphate and phenol are formed.

0.9753 gram substance gave 1.0086 gram $BaSO_4$ (Carius).

	Calculated for $Ba(OSO_2NHC_6H_5)_2$.	Found.
S	13.30	13.28

The reaction between aniline and ethyl chlorsulphate is consequently to be interpreted as follows: The ethylidene particles alkylate the aniline, giving chiefly ethylaniline[2] and only traces of higher alkylated products, and these unite at once with the hydrogen chloride to form salts. The sulphur trioxide (2 molecules) reacts with aniline to form phenylimidodisulphonic acid,

$$C_6H_5N\begin{matrix}H\\H\end{matrix} + 2O{-}SO_2 \rightarrow C_6H_5N\begin{matrix}SO_2OH\\SO_2OH\end{matrix},$$

and this, on treatment with water, is split into equal molecules of sulphuric and phenylsulphamic acids. From these data it is clear that aniline, on treatment in the cold with chlorsulphonic acid or with sulphur trioxide, must first give phenylimidodisulphonic acid. This is very probable from

[1] Traube: Ber. d. chem. Ges., **23**, 1653.
[2] Cf. Claesson and Lundvall: *Ibid.*, **13**, 1699.

the following: Chlorsulphonic acid was allowed to act, at low temperatures, on a chloroform solution containing 3 or more molecules of aniline. The resulting precipitate, on treatment with aqueous barium hydroxide, gave large amounts of barium sulphate besides phenylsulphamic acid. Similar results are obtained when carefully prepared sulphur trioxide is added to an excess of aniline in the cold.

Taking into consideration the fact that ethyl chlorsulphonate, chlorsulphonic acid, and sulphur trioxide all give, on treatment with aniline, phenylimidodisulphonic acid, or its products of hydrolysis, and that these reagents also give with dimethylaniline the same product, namely dimethylaniline sulphurtrioxide, we have in both instances a virtual demonstration of the presence of active sulphur trioxide particles.

The Action of Ethyl Chlorsulphonate on Alcohol and Sodium Alcoholates.

The action of ethyl chlorsulphonate on alcohol was one of the first reactions of this substance to be investigated. Some controversy arose as to the nature of the products formed, but it finally became evident that there are varying proportions of hydrogen chloride, ethyl chloride, ethyl ether, sulphuric acid, and primary and secondary ethyl sulphate. The formation of all these substances is now self-evident; the dissociation-products of ethyl chlorsulphonate—ethylidene, hydrogen chloride, and sulphur trioxide—must naturally act with the alcohol as follows: The sulphur trioxide adds the alcohol, giving primary ethyl sulphate, which is then partly converted by the ethylidene into diethylsulphate. The hydrogen chloride is in part absorbed by ethylidene, giving ethyl chloride, and some of the ethylidene naturally unites with the alcohol present in excess to give ether.

It must, however, be emphasized here that ethyl chlorsulphonate and sodium alcoholates give, in absolute ethereal solution, soluble and very stable addition-products, which were first observed by Bushong, and whose properties are discussed in the introduction. They are, moreover, as shown by Bushong, decomposed at once by addition of cold water,

giving varying quantities of alkyl ethyl sulphate, alkyl sodium sulphate, sodium sulphate, alkyl ethyl oxide, and alkyl hydroxide.

Behavior of Ethyl Chlorsulphonate on Heating.

From the properties of ethyl chlorsulphonate described above, it follows that this substance must possess a very low point of dissociation.[1] This was found to be the case. When small quantities of ethyl chlorsulphonate are quickly distilled at ordinary pressure it boils approximately, but with noticeable decomposition, at about 152°. If, however, the substance is heated in a bath kept at 160°, decomposition sets in rapidly, as shown by what follows: Thirty grams of ethyl chlorsulphonate were placed in a flask with a long neck, which was connected in series with a Bunsen wash-bottle containing sodic hydroxide, a small tube containing bromine and water, and an azotometer. The flask was now heated in an oil-bath, the temperature of which was kept at 160°. The ester gradually darkened and evolved gas until only a tarry mass containing some free sulphuric acid was left. As soon as the air was expelled no bubble of gas passed beyond the bromine tube. The sodic hydroxide solution had gained 8.5 grams in weight, of which 6.2 grams increase was found to be due to absorbed hydrogen chloride (theory, 7.58 grams) and the remainder to sulphur dioxide. Seven and five-tenths grams of ethylene bromide, or 20 per cent of the theoretical amount, were found in the bromine tube.

Sulphur dioxide, sulphuric acid, ethylene (20 per cent), hydrogen chloride (80 per cent), and carbonaceous matter are therefore the products of decomposition of ethyl chlorsulphonate under the given conditions.

These results are self-evident from the standpoint of a dissociation into ethylidene, hydrogen chloride and sulphur trioxide, especially when one considers the experiments of Nef on the dissociation of alkyl sulphates, alkyl potassium sulphates, and alkyl haloids.[2]

[1] Cf. Nef: Ann. Chem. (Liebig), 318, 40–50.
[2] *Ibid.*, 318, 1–57.

The sulphur dioxide results from the abstraction of oxygen from sulphur trioxide,

$$OSO_2 \rightleftarrows O + SO_2,$$

by ethylidene, and the resulting acetaldehyde is immediately polymerized and carbonized by more sulphur trioxide with formation of some sulphuric acid. Twenty per cent of the ethylidene is transformed, by intramolecular alkylation,[1] into ethylene.

Another experiment with 25 grams of ethyl chlorsulphonate was carried out in the presence of 20 grams of powdered tin and a trace of iodine. The apparatus was similar to that used in the former experiment, but a condenser and receiver were inserted between the caustic soda wash-bottle and the distilling-flask. On heating to 130°, ethylene, sulphur dioxide, and small amounts of hydrogen chloride were evolved and 4 cc. of tin tetrachloride were collected in the receiver. The stannic chloride was identified by its boiling-point and its chemical reactions.

This chlorination of the tin by the ethyl chlorsulphonate is easily understood because of the known properties of chlorsulphonic acid—which, as has been shown, is a dissociation-product of the ester.

Chlorsulphonic acid breaks down when heated in a sealed tube to 170° to 180°, giving equal molecules of sulphuric acid and sulphuryl chloride,[2]

$$2ClSO_3OH \longrightarrow SO_2Cl_2 + SO_2(OH)_2.$$

More recently Wohl and Ruff[3] have shown that the same decomposition takes place at 70° in the presence of catalyzers, such as aluminium chloride, iodine chloride, etc. I have found that a chloroform solution of chlorsulphonic acid, containing traces of iodine, will dissolve metallic tin in the cold with brisk evolution of sulphur dioxide and formation of stannic chloride.[4] This reaction can also be explained on the

[1] Nef: Ann. Chem. (Liebig), 318, 13.
[2] Behrend: Ber. d. chem. Ges., 8, 1004.
[3] *Loc. cit.*
[4] Cf. Heumann and Köhlin: Ber. d. chem. Ges., 15, 416.

basis of a dissociation of chlorsulphonic acid into sulphur trioxide and hydrogen chloride and subsequent decomposition of the hydrogen chloride by the stannous chloride with formation of stannic chloride and atomic hydrogen, which is at once absorbed by the sulphur trioxide molecules present to give sulphur dioxide and water. It does not, therefore, necessarily involve an intermediate transformation of chlorsulphonic acid into equal molecules of sulphuric acid and sulphuryl chloride.

Ethyl Chlorsulphonate and Sodium Acetoacetic Ester.

The reaction of ethyl chlorsulphonate with the sodium salt of malonic ester and acetoacetic ester, respectively, has already been referred to in the introduction; contrary to expectation, no alkylation takes place. The ethyl chlorsulphonate acts as a chlorinating agent in both cases. Similar results have been observed previously by Nef in the case of cyanogen bromide and iodide, as well as in the case of brom- and iodphenylacetylene. Analogous results have also since been obtained by Brühl with benzenesulphonechloride and by Findeisen with *p*-tolylsulphone chloride. There is no doubt that carbon tetrachloride, bromide, and iodide, as well as all nitrogen halogen compounds, will give similar results on treatment with sodium malonic ester and allied compounds. The theory of the reaction has been exhaustively discussed by Nef[1] and is briefly presented in the introduction.

To 58.8 grams of sodium acetoacetic ester, suspended in absolute ether, and cooled in a freezing-mixture, 26.7 grams of ethyl chlorsulphonate (0.5 molecule) were added. The reaction takes place quietly. After two hours' standing the ether was decanted, and the sticky precipitate removed, and well washed by kneading with ether in a mortar.

The ether was found to contain 33 grams of oil, which consisted of about equal parts of acetoacetic ester and α-chloracetoacetic ester, besides small amounts of diacetsuccinic ester. These were separated by shaking with cold 10 per cent sodium carbonate solution by which only the α-chlor-

[1] Ann. Chem. (Liebig), **308**, 301–307.

acetoacetic ester is dissolved. It is then recovered from the alkaline solution by acidifying with dilute sulphuric acid and extracting with ether. The sticky precipitate, insoluble in ether, was dissolved in water and found to contain some soluble sulphate, besides a large amount of sulphite and alcohol; the residue therefore consisted chiefly of sodium ethyl sulphite with some sodium sulphate.

Copper acetoacetic ester and ethyl chlorsulphonate do not react at ordinary temperatures in benzene solution. On heating the mixture under a reflux condenser, cuprous chloride is gradually formed. The filtrate, after getting rid of benzene, gave a dark, sticky, non-volatile gum, from which it was impossible to isolate a definite product.

Ethyl Chlorsulphonate and Sodium Malonic Ester.—Fifty-seven grams of sodium malonic ester, suspended in cold absolute ether, were treated with 22.5 grams of ethyl chlorsulphonate (0.5 molecule). The reaction takes place rapidly but without marked rise in temperature. The mixture was heated for a short time on a water-bath and the ether then poured off from the sticky precipitate, which was handled as in the case of sodium acetoacetic ester. The ether solution gave, on fractionation under reduced pressure, 8 grams of malonic ester and 20 grams of a snow-white solid. The latter, on crystallization from ligroin, was identified as acetylenetetracarboxylic ester, $(COOR)_2CH—CH(COOR)_2$, melting at 75° and boiling at 205° to 208° under 42 mm. pressure. It was carefully compared with a known sample kindly loaned me by Dr. Nef.

The sticky precipitate, 31.5 grams, insoluble in ether, was found to contain only traces of sulphate. It obviously contained chiefly sodium chloride and sodium ethyl sulphite. The main portion was treated with dilute sulphuric acid when much sulphur dioxide was set free. The solution, which contained no perceptible amount of malonic ester, was distilled, and the first portions of the distillate gave, on treatment with solid potassium carbonate, 2 cc. of ethyl alcohol, which was identified by conversion into ethyl benzoate.

The Reactions of Ethyl Hypochlorite.

Finally, it may be of interest to state in this connection that very careful experiments with large amounts of ethyl hypochlorite and sodium ethylate, using dry ligroin as a diluent, have shown that reaction takes place almost instantly at 0°, but no trace of ethyl ether[1] or of diethyl hyperoxide is formed.

According to the observations of Bushong, made while in this laboratory, ethyl hypochlorite acts with sodium phenolate and sodium acetoacetic ester as a chlorinating agent. The same is true, as I have found, in the case of diethylamine and trimethylethylene, *i. e.*, chlordiethylamine, $(C_2H_5)_2NCl$, and chlorisoamylene, besides ethyl alcohol, are formed.

These observations, therefore, show that ethyl hypochlorite does not act here as an alkylating but as a chlorinating agent; the latter property is naturally to be explained on the same basis as the reactions of ethyl chlorsulphonate just presented.

Ethyl Chlorsulphonate and Sodium Phenolate.—In view of the striking analogy often existing between the reactions of sodium acetoacetic ester and those of the sodium salts of phenols, it seemed of especial interest to determine whether ethyl chlorsulphonate would behave towards sodium phenolate as a chlorinating or as an alkylating agent. The experiment was carried out and the reaction found to be analogous to those obtained with free alcohols and with sodium alcoholates, *i. e.*, only alkylation takes place.

The action of ethyl chlorsulphonate on phenol has been mentioned by Purgold,[2] who, however, obtained no definite results.

Fifty grams of dry sodium phenolate, prepared by mixing alcoholic solutions of carbolic acid and sodium ethylate, and distilling off the alcohol in an atmosphere of hydrogen, were finely powdered, suspended in absolute ether, and cooled with ice-water. Thirty-one grams of ethyl chlorsulphonate (0.5 molecule) were thereupon added, and the mixture shaken until

[1] Cf. Nef: Ann. Chem. (Liebig), **298**, 323-324; **318**, 47-48.
[2] Ber. d. chem. Ges., **6**, 502.

the odor of the ester had disappeared. The salt residue, insoluble in ether, weighed 31 grams and was found to contain 29.1 per cent of sodium, 20 per cent of chlorine, and 15.76 per cent of sulphur (precipitated as barium sulphate). It gave a strongly acid reaction and obviously consisted only of sodium chloride and primary sodium sulphate. The ether solution gave 46 grams of oil, which, by separating with aqueous sodic hydrate, was proved to consist of 22 grams of phenetol, $C_6H_5OC_2H_5$, and 24 grams of carbolic acid. The phenetol boiled at 172° and, by heating in a sealed tube with hydriodic acid, was decomposed into ethyl iodide and phenol.

In conclusion, I take great pleasure in gratefully acknowledging my obligations to the inspiring example and advice of Dr. Nef in the prosecution of this work.

USE OF THE CHROMATES OF BARIUM AND OF SILVER IN THE DETERMINATION OF SULPHATES AND CHLORIDES.

By Launcelot W. Andrews.

Several years ago a method was described by the author[1] for the volumetric determination of sulphates, of which the leading features may be recalled in outline here. A reagent, prepared by dissolving barium chromate in dilute hydrochloric acid, was added to the sulphate solution, the liquid was then neutralized, and, after filtration, the chromate in the filtrate titrated iodometrically in the usual manner. The amount of chromate so found was equivalent to the sulphate originally present.

This process is both accurate and rapid, as shown by my own observations and those of others.[2] It suffers, however, from a rather serious drawback, namely, that a solution of barium chromate in hydrochloric acid of the prescribed concentration does not keep perfectly,[3] a fact overlooked at the time of the publication of my first paper referred to above,

[1] This Journal, **11**, 567 (1889).

[2] Marchlewski: Fres. Ztschr. **32**, 316 (1893); Reuter: Chem. Ztg., **22**, 357 (1898); compare also Stolle: Ztschr. angew. Chem., 1892, p. 234.

[3] A. von Asboth: Chem. Ztg., **16**, 922 (1892).

owing to the fact that I had not then had occasion to work with solutions which had been kept more than ten days. Hydrochloric acid is, nevertheless, gradually oxidized by chromic acid, even in solutions far more dilute than the weakest which could be practically used for dissolving barium chromate, although weeks, months, or years may be requisite to make the action very apparent.

To overcome this difficulty, which has doubtless stood in the way of a more general employment of the method in question, it is obviously necessary to substitute for the hydrochloric acid some other acid which will not be capable of oxidization by chromic acid, which will not itself be either an oxidizing or a reducing agent in its action on hydriodic or chromic acids, and which will be sufficiently strong to dissolve the requisite amount of barium chromate. As possessing these qualifications two acids come into consideration in the first rank, *i. e.*, trichloracetic and perchloric acids. The latter would probably be extremely well suited to the purpose, but it cannot, at present, be obtained by purchase in a sufficiently pure state, that is, free from hydrochloric acid and from all lower acids of chlorine.

Trichloracetic acid meets all requirements as to resisting the action of chromic acid, and it can be purchased in the pure state without trouble. A normal solution of this acid is capable of dissolving the finely divided barium chromate rather freely but not very rapidly. The solution may be aided by the application of gentle heat, but caution must be observed in this direction in order to avoid too extensive hydrolysis. Thus, a normal solution of trichloracetic acid was agitated with an excess of barium chromate at about 90° for a few minutes, free evolution of carbon dioxide and chloroform occurring. The liquid was then cooled and allowed to stand for three days at the temperature of the room.

A slight recrystallization of the barium chromate had taken place. The liquid now contained in each cubic centimeter 126 milligrams of trichloracetic acid and 24 milligrams of barium chromate. On further standing, an increased deposition of the chromate was observed. For practical purposes it

may be assumed that in concentrations between normal and seminormal, trichloracetic acid is capable of maintaining permanently in solution one-sixth of its own weight of barium chromate. Observations on this solution have now continued six months and no change has been noted that in any way influences the analytical results obtained with it. Of course, the hydrolysis of the trichloracetic acid goes on, but this change is slow and has absolutely no bearing, since the solution is not employed as a standard and is always used in excess.

This modification entirely does away with the only objection to the method in its original form. No other change is required beyond the substitution of trichloracetic for hydrochloric acid, so that for all details reference may be made to the former paper (*loc. cit*).

Since the question of priority has been raised concerning the original method as between myself and Quantin, I desire to state what the facts are that bear on the history of the process. My method was described in a paper read before the Iowa Academy of Sciences in Des Moines, Dec. 27, 1887,[1] which was published in this JOURNAL in 1889.[2] Quantin published in 1889[3] a somewhat similar process, of which the following are the features: Equal volumes of equivalent standard solutions of potassium dichromate and of barium chloride are mixed with sufficient hydrochloric acid to keep the barium chromate from separating. This liquid is added to the sulphate solution, then ammonia to alkaline reaction, and, after filtration, the chromate in solution is titrated by standardized ferrous sulphate, using potassium ferricyanide as indicator of the end of the reaction. Quantin had previously published practically the same method in 1886.[4] It will be seen that Quantin's method differs from mine not only in the choice of titration by ferrous solution, but in the far more important particular that two or three[5] titrated solutions

[1] The proceedings of this meeting were not published till 1890.
[2] *Loc. cit.*
[3] Bull. soc. chim., [3], 1, 21 (1889).
[4] Moniteur scientifique, 1886, p. 1222; also reprinted in Chem. News, 54, 233.
[5] Two in the modified, three in the first process (1886).

are demanded by his process, whereas only one is used in mine, because in the latter the proper relation between barium and chromic acid is secured by starting with pure barium chromate instead of placing dependence upon a preliminary analytical process to secure this end. Hence the former method always demands a correction, variable in each case. Naturally, if I had been aware of Quantin's publications I would not have omitted to mention them, but at the time his second paper had not reached this country and his first was not mentioned in publications available to me. As a matter of fact, the only points in common to the essentially different methods is that both make use of barium and of chromic acid salts.

It appears as if the principle, peculiar to my method, of using a reprecipitable salt is capable of more extended application, as for instance to the determination of chlorides. Thus, if silver chromate is added to a solution of a chloride, an equivalent amount of chromate passes into solution in accordance with the equation

$$2MCl + Ag_2CrO_4 = M_2CrO_4 + 2AgCl,$$

and a colorimetric or volumetric[1] titration of the chromate allows a conclusion as to the amount of the chloride, bromide, etc., originally present. The feasibility of this scheme has been tested under my direction by Mr. H. V. Farr, who has obtained excellent results. A new volumetric method for determining chlorides is hardly a desideratum, perhaps, but a good colorimetric method for estimating traces of chlorides, as for example, in water analysis, cannot be regarded as superfluous. The experiments have demonstrated that it is not necessary to bring the silver chromate into solution by any acid. It is sufficient to agitate the finely divided and carefully prepared salt with the highly dilute chloride solution, then to filter or decant, and compare the depth of color of the clear liquid with that of a suitable series of types made by dissolving known amounts of potassium monochromate in water. These type solutions keep indefinitely. The process

[1] Compare De Konninck and Niboul: Ztschr. f. angew. Chem., 1891, p. 295.

is much more rapid than any titration method, and for the most dilute solutions is at least as accurate. It is expected to follow this preliminary notice of the method by a more detailed account.

CHEMICAL LABORATORY,
STATE UNIV. OF IOWA,
July 13, 1904.

Contributions from the Chemical Laboratory of the University of Cincinnati.

METHODS FOR THE DETECTION OF ACETATE, CYANIDE, AND LITHIUM.

BY STANLEY R. BENEDICT.

A method for the detection of acetates, much more delicate than those in common use, or than any of which I have been able to find record, can be based upon the two well-known facts (1) that unlike most weak acids, acetic acid has a soluble silver salt, and (2) that the acidity or degree of ionization of acetic acid is greatly reduced by the presence of an acetate.

The solution, freed from all cations except those of the sodium group, is made just alkaline with sodium carbonate. An excess of silver nitrate solution is now added and the precipitate filtered off, the solution being thus left perfectly neutral. The excess of silver is removed with a little normal sodium chloride solution. The filtered solution is now saturated with hydrogen sulphide.

In another test-tube 2 cc. normal cobalt nitrate are acidulated with 2 or 3 drops normal acetic acid and saturated with hydrogen sulphide. A small amount of cobalt sulphide will usually be precipitated, but may be disregarded.

Upon mixing the two solutions thus prepared a heavy black precipitate of cobalt sulphide will be obtained immediately if the test solution contains acetate. This test is capable of detecting acetate in a N/500 solution of sodium acetate. It is applicable in presence of all strong acids and of all weak acids having insoluble silver salts.

The following method for the detection of cyanides in presence of sulphocyanates and ferrocyanides is reliable and extremely delicate. It has the advantage over the best methods

hitherto proposed of avoiding the somewhat cumbersome expedient of distillation. It is based upon the action of cyanides upon the freshly precipitated oxides of mercury. As the method was first worked out, a solution of a mercuric salt was made alkaline with sodium hydroxide and the solution to be tested was added. It was found that in presence of cyanide the yellow precipitate of mercuric oxide dissolved (presumably with formation of a complex cyanide). Neither sulphonor ferrocyanides show this solvent action upon mercuric oxide.

The solvent action of cyanides is so marked that a portion of the precipitate formed, upon treating 1 cc. of N/25 mercuric chloride solution with sodium hydroxide, can be seen to dissolve when treated with a few cubic centimeters of a N/2000 solution of potassium cyanide. Of course, the full delicacy of the test could best be secured by filtering off any precipitate remaining after adding the solution to be tested, acidifying the filtrate, boiling, and testing for mercury with hydrogen sulphide.

It has, however, been found, that the action of cyanides upon mercurous oxide can be made the basis of a more delicate and desirable test than the one above proposed.

If a solution of mercurous nitrate be precipitated with an excess of sodium hydroxide, and potassium cyanide solution then be added, a portion of the precipitate dissolves, while the color of that which remains is changed from black to light gray. The action of the cyanide is to cause a portion of the mercurous oxide to be reduced to metallic mercury with the formation of a corresponding amount of mercuric oxide, which is then dissolved by the cyanide present. The gray precipitate remaining can readily be shown to be metallic mercury. Vitali[1] showed that hydrocyanic acid has this action upon calomel and some other mercurous salts. The mercurous oxide is in nowise affected by either ferrocyanides or sulphocyanates. In order to obtain the full delicacy of the test it should be made as follows:

The solution to be tested is made alkaline with sodium hy-

[1] O. Vitali: L'Orosi, **15**, 186; J. Chem. Soc., **62**, 1416 (1892).

droxide, then about 0.5 to 1 cc. of N/25 mercurous nitrate is allowed to flow slowly down the side of the tube so that it will remain upon the top. A ring of black mercurous oxide is thus formed. The test-tube is now gently agitated so that a mixture of the precipitate with the solution slowly takes place. If cyanide be present, a portion of the precipitate will dissolve while the rest will become light gray in color.

When made as above described this test is extremely delicate, readily detecting CN in 5 cc. of a solution containing about 1 part CN in 1,000,000 parts of solution. This is not the limit of its delicacy. When it is remembered that the limit of the Prussian blue test for cyanide is placed by Link and Moeckel[1] at 1 part in 50,000, it will be seen that this test is not at all lacking in delicacy.

When the test is made, not by the contact method as described but by simply adding the mercurous nitrate to the alkaline test solution, there is a possibility, when the proportion of mercurous nitrate used is small, of mistaking the small quantity of black mercurous oxide, distributed through the liquid, for the gray mercury, whose formation constitutes the test, but no such confusion can arise if the above directions are adhered to. For the most delicate work a blank test with pure sodium hydroxide may be made for comparison, the same proportions of mercurous nitrate and sodium hydroxide being used as in the test.

While ferricyanides would interfere with this test, it will be remembered that cyanides are oxidized by these, so that it is unnecessary to test for cyanides when ferricyanides are present.

The detection of lithium in the presence of sodium without the aid of the spectroscope is attended with considerable difficulty. Of the precipitation methods so far proposed, practically only one can be of any service, *viz.*, the precipitation as phosphate in alkaline solution. Yet this method, as hitherto proposed, can be applied only where lithium is present in considerable amount, say not less than a N/8 solution. By the modification of this method described below, it is pos-

[1] Link and Moeckel: Ztschr. anal. Chem., 17, 456 (1878).

sible to obtain a distinct precipitate with a N/100 solution of lithium chloride, this being about the limit of its availability. This modification depends upon the fact that the precipitate of lithium phosphate is much less soluble in dilute alcohol (whether hot or cold) than in water, while sodium phosphate, although precipitated by dilute alcohol, readily redissolves upon heating. The procedure is as follows: A little ammonium hydroxide is added to the solution to be tested, then about one-tenth volume of N/5 disodium hydrogen phosphate is added, and finally enough ethyl alcohol to produce a fairly heavy precipitate, which remains permanent upon shaking the tube. This precipitate may consist of only sodium phosphate, or may be a mixture of sodium phosphate and lithium phosphate. The solution is now heated to boiling. If lithium be absent the precipitate will completely dissolve, leaving a perfectly clear solution; if, however, lithium be present it will be precipitated upon warming, and the precipitate will not dissolve even upon hard boiling. If the amount of lithium be small the solution will first clear and the precipitate will form upon boiling. Salts of potassium and ammonium do not interfere.

ON THE RATE OF CRYSTALLIZATION OF PLASTIC SULPHUR.

By J. H. Kastle and Walter Pearson Kelley.

The fact that plastic sulphur gradually changes into the crystalline variety of the element has been known for a long time. According to Dumas[1] this change usually requires from twenty-four to thirty-six hours. It has also been observed to vary with the temperature. According to Regnault[2] the change is so rapid at 100° that the thermometer shows a rise of temperature of from 10° to 12°. According to Daguin[3] the crystallization of plastic sulphur always begins in the center of the mass or in the axis of the cylinder, that is, at the point where the cooling has been slowest. He

[1] Ann. chim. phys., [2], **36**, 83 (1821).
[2] *Ibid.*, [3], **1**, 205 (1841).
[3] Compt. rend., **20**, 1665 (1845).

concludes, therefore, that the more rapid the cooling of the sulphur the slower the crystallization. He also observed that sunlight greatly accelerates the rate of crystallization, and that the higher the temperature at which the sulphur had been poured the slower its conversion into the crystalline modification.

According to Deville[1] plastic sulphur is a mixture of sulphur which is soluble in carbon bisulphide and an insoluble variety. In one specimen of plastic sulphur he found 35 per cent of the insoluble form. This insoluble portion he found to be remarkably stable at ordinary temperatures, showing no tendency to crystallize even after four years. On the other hand, when heated to 100° it soon changed to the crystalline variety. More recently Gernez[2] made a study of the rate of change of supercooled sulphur into the crystalline varieties. His method consisted in fusing octahedral sulphur in a graduated U-tube of 2 mm. bore, at a definite temperature, and for a certain definite length of time. The tube containing the fused sulphur was then immersed in a bath, the temperature of which was below the melting-point of sulphur. A small crystal of prismatic or octahedral sulphur was then dropped into the U-tube and the time required for the solidification of the sulphur through a constant distance of 10 mm. determined. It was found that sulphur that had been heated to 170° required a considerably longer time for solidification than that which had been fused at lower or higher temperatures. According to this observer this is in harmony with the observations of Berthelot, who found that at 170° the greatest amount of insoluble sulphur is produced. Gernez also observed that the phenomena attending the solidification of supercooled sulphur are more complicated than in the case of phosphorus, the difference being probably due to the fact that amorphous phosphorus is insoluble in the fused ordinary variety, whereas the different modifications of sulphur remain mixed together in the fused mass.

Several years ago the attempt was made by Mr. H. P. Bas-

[1] Compt. rend., **26**, 119 (1848).

[2] *Ibid.*, **95**, 1278–1280; **97**, 1298–1301, 1366–1369, 1433–1435, 1477–1480; **98**, 144–146; **100**, 1584–1585.

sett[1] and one of us (Kastle) to determine the rate of change of plastic sulphur into the crystalline variety, by determining the amount of soluble and insoluble sulphur remaining in certain specimens of plastic sulphur at the end of certain intervals after its preparation. The method was not found to lend itself particularly well to these determinations, however, and the attempt was abandoned. Later it occurred to us that more reliable results might possibly be obtained by the specific gravity and dilatometric methods. The results of these measurements are given in the following pages:

Experiment 1.

Sulphur heated to 200° and poured into cold water. The specimen was then kept in water, at ordinary temperature, during the several intervals indicated below:

	Grams.	Specific gravity.[2]	Per cent changed.
Weight in water when poured	2.144	1.923	0
" " " 1 hour later	2.168	1.943	15.7
" " " 1 " "	2.192	1.963	31.4
" " " 3 hours "	2.2038	1.973	39.2
" " " 4 " "	2.2125	1.981	45.6
" " " 5 " "	2.2195	1.987	50.3
" " " 6 " "	2.2252	1.992	54.3
" " air	4.4665		

Another specimen of the same pouring was kept in water at 70° for certain intervals indicated below, with the following results:

	Grams.	Specific gravity.	Per cent changed.
Weight in water after being heated 1 hour	2.249	2.021	77.1
Weight in water after being heated 2 hours	2.261	2.032	850.
Weight in water after being heated 3 hours	2.262	2.33	86.6
Weight in water after being heated 4 hours	2.270	2.04	92.1
Weight in water after being heated 5 hours	2.275	2.045	96.0
Weight in air	4.451		

[1] Thesis for the degree of B. S., 1901.

[2] The specific gravity of the sulphur was determined in every case by weighing the specimen, suspended by a fine silk thread, in a beaker of distilled water at ordinary temperatures.

Experiment 2.

Another experiment was carried out with sulphur which had been heated to 444° before pouring. One portion of this specimen was heated to 80°, another to 60°, and another to 40°. The one heated to 80° showed the following results:

	Grams.	Specific gravity.	Per cent changed.
Weight in water after being heated 1 hour	0.8328	2.935	76.7
Weight in water after being heated 2 hours	0.8395	2.039	79.1
Weight in water after being heated 4 hours	0.8465	2.07	100.0
Weight in air	1.6373		

The specimen heated to 60° showed the following:

	Grams.	Specific gravity.	Per cent changed.
Weight in water after being heated 1 hour	1.7425	1.958	25.0
Weight in water after being heated 2 hours	1.7477	1.964	28.8
Weight in water after being heated 4 hours	1.756	1.973	34.9
Weight in air	3.5602		

The specimen heated to 40° showed the following:

	Grams.	Specific gravity.	Per cent changed.
Weight in water after being heated 1 hour	2.1275	1.936	11.6
Weight in water after being heated 2 hours	2.1603	1.944	33.3
Weight in water after being heated 4 hours	2.1838	1.985	49.6
Weight in air	4.3992		

The initial specific gravity of the sulphur used in Experiment 2 was found to be 1.921.

Experiment 3.

In this experiment the sulphur was heated to boiling and poured at 444° into cold water. The specimen was then kept under cold water for certain intervals, at the end of

which the specific gravity was determined with the following results:

	Gram.	Specific gravity.	Per cent changed.
Weight in water when poured	0.4425	1.952	0
" " " 1 hour later	0.449	1.979	25.0
" " " 2.5 hours later	0.457	2.015	58.3
" " " 5 " "	0.463	2.042	83.3
" " " 6.5 " "	0.465	2.051	91.6
" " " 7.5 " "	0.466	2.056	96.3
" " " 24 " "	0.467	2.06	100.0
" of sulphur in air	0.9072		

Experiment 4.

Conditions similar to those in Experiment 3.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.7841	1.947	0
" " " 6 hours later	0.7841	1.947	0
" " " 7.5 " "	0.7868	1.955	11.1
" " " 8.5 " "	0.791	1.965	25.0
" " " 11 " "	0.8021	1.992	62.5
" " " 12 " "	0.805	1.999	72.2
" " " 24 " "	0.8129	2.019	100.0
" " air	1.6105		

Experiment 5.

Conditions same as in Experiments 3 and 4.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.7325	1.919	0
" " " 3 hours later	0.7325	1.919	0
" " " 4.5 " "	0.7344	1.923	3.2
" " " 28 " "	0.746	1.952	26.4
" " " 30 " "	0.7596	1.986	53.6
" " " 31.5 " "	0.7646	1.999	64.0
" " " 33 " "	0.7708	2.015	76.8
" " " 35 " "	0.774	2.024	84.0
" " " 51 " "	0.7813	2.044	100.0
" " air	1.5295		

These results undoubtedly indicate that the rate of change of plastic into crystalline sulphur varies according to the temperature at which the sulphur is poured; in other words, it diminishes with the degree of the supercooling, and also with the temperature at which it is preserved. The higher the

temperature the more rapid the change. It should be noted further that our results do not seem to accord with those of Gernez. The amount of slowly changing sulphur formed in any particular specimen seems to be proportional to the initial temperature to which the sulphur is heated. Indeed in all of our work we have never obtained any evidence whatsoever that it reaches a maximum at 170°. In fact all specimens of sulphur which were poured at temperatures below 200° were found to change too rapidly to be measured by the methods here employed. It is also a matter of common experience that specimens of plastic sulphur, prepared by pouring boiling sulphur into cold water, crystallize much more slowly than those prepared at lower temperatures.

Effect of the Medium on the Crystallization of Plastic Sulphur.

In our earlier work with Mr. Bassett we got the impression that certain solvents exercise an accelerating influence on the crystallization of plastic sulphur. In order to throw more light on the subject the following experiments were carried out. A specimen of plastic sulphur was divided into several portions. One of these was kept under dilute ammonium hydroxide, a second under 95 per cent alcohol, a third under dilute bromine water, and a fourth under N/10 iodine solution. For the sake of comparison, another portion of the same specimen was kept under water for the desired intervals. The specific gravities of these several specimens were determined at the end of certain intervals, in the usual manner, with the following results:

In Water.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.7925	1.934	0
" " " 1 hour later	0.793	1.935	0.8
" " " 2 hours "	0.7983	1.947	10.8
" " " 3 " "	0.8095	1.972	31.6
" " " 4 " "	0.8225	2.005	59.1
" " " 5 " "	0.832	2.029	79.1
" " " 6 " "	0.8363	2.039	87.5
" " " 7 " "	0.8383	2.04	88.3
" " " 23 " "	0.842	2.054	100.0
" " air	1.6405		

In Dilute Ammonium Hydroxide.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.8545	1.944	0
" " " 1 hour later	0.8595	1.955	12.2
" " " 2 hours "	0.872	1.982	42.2
" " " 3 " "	0.8858	2.013	76.6
" " " 4 " "	0.8952	2.034	100.0
" " air	1.7595		

In Alcohol.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.6567	1.949	0
" " " 1 hour later	0.6567	1.949	0
" " " 2 hours "	0.666	1.977	24.5
" " " 3 " "	0.6805	2.019	61.4
" " " 4 " "	0.69	2.048	86.8
" " " 5 " "	0.6943	2.061	98.2
" " " 6 " "	0.695	2.063	100.0
" " air	1.3482		

In Bromine Water.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.5588	1.936	0
" " " 1.5 hours later	0.575	1.99	36.4
" " " 3 " "	0.5752	1.991	37.1
" " " 8 " "	0.5957	2.064	86.4
" " " 23 " "	0.6012	2.084	100.0
" " air	1.1555		

In N/10 Iodine Solution.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.6442	1.908	0
" " " 2 hours later	0.645	1.911	2.1
" " " 3 " "	0.6458	1.913	3.7
" " " 8 " "	0.652	1.93	16.4
" " " 23 " "	0.668	1.975	50.0
" " " 27 " "	0.669	1.978	52.2
" " " 28 " "	0.6807	2.012	77.6
" " " 32 " "	0.6835	2.02	84.3
" " " 43 " "	0.6905	2.042	100.0
" " air	1.353		

It will be observed that ammonia, alcohol, and bromine ac-

celerate the crystallization of plastic sulphur. On the other hand, iodine retards the crystallization to a very marked degree. The last result is in harmony with an observation by Dietzenbacher,[1] who found that by adding 1/400 of its weight of iodine to molten sulphur at 180°, or even lower, a variety of sulphur was obtained which remained plastic for a very long period and which was entirely insoluble in carbon bisulphide.

Plastic Sulphur Has No Definite Melting-point.

All that is known concerning plastic sulphur seems to indicate that it is a supercooled liquid containing one, or probably several, molecular species of the element. It seemed desirable, therefore, to study more closely the effect of heat on the substance with the view of determining whether or not it has a definite melting-point. In order to determine this some fine strands of plastic sulphur were obtained by pouring sulphur, that had been heated to boiling, into cold water. A short cylindrical piece of this was introduced into a melting-point tube and heated gradually in a sulphuric acid bath. At 60° the sulphur was observed to take on a peculiar, dull, roughened appearance. At 90° it became perfectly clear and transparent, and at 109° it began to flow down the walls of the tube. At 114° it was entirely liquid, although considerably darker than molten sulphur that had been prepared by melting the crystalline variety of the element at this temperature. Another specimen of the same plastic sulphur was placed in a melting-point tube and plunged into boiling water. At the end of ten minutes it began to flow, and shortly thereafter changed suddenly to the crystalline variety. It has also been observed that when a quantity of plastic sulphur is suspended by means of a silk thread in boiling water, it begins to flow and soon separates from the thread and drops to the bottom of the vessel. We see, therefore, that plastic sulphur passes into the perfectly liquid form through insensible gradations of temperature; in other words, as is to be expected, it possesses no definite melting-point, the effect of any increase of temperature being simply

[1] Compt. rend., **56**, 39 (1863).

to diminish its viscosity and to increase its tendency to pass to the crystalline forms of the element.

In this connection a very interesting result was obtained. A cylindrical piece of plastic sulphur that had been prepared by pouring boiling sulphur into cold water was placed in a small test-tube. The bottom of the tube was then gently heated in such a manner as to melt the lower end of the sulphur throughout about one-fourth of its length, taking the precaution to preserve the continuity of the fused and unmelted portions. On removing the source of heat, that portion of the sulphur that had been melted, crystallized almost immediately, whereas the unmelted portion remained plastic and perfectly transparent for several hours.

Color Changes in Plastic Sulphur Brought About by Heat.

It is well known that the development of the plastic condition in sulphur is accompanied by marked changes in color, and just as the plasticity persists for a time after cooling, so also the reddish-brown tints resulting from the application of heat are preserved in the specimen for some time after cooling. The one change is always the concomitant of the other, and both are doubtless the outward signs of the same molecular change in liquid sulphur. It is an easy matter to predict the stability of any particular specimen of plastic sulphur from the color alone. As a rule, light, amber-colored specimens of plastic sulphur crystallize easily, whereas reddish-brown varieties remain plastic for longer periods.

Such being the case, it occurred to us that it would not be without interest to study the changes in color of plastic sulphur brought about by heat. In order to do this two melting-point tubes were attached to the same thermometer. In one of these was placed a short cylindrical piece of plastic sulphur, which had been prepared by pouring boiling sulphur into cold water, and which was clear and transparent, and of a reddish-brown color. A few small crystals of orthorhombic sulphur were placed in the second tube, and the thermometer with the tubes attached was placed in a bath of pure sulphuric acid, and the whole gradually heated over a small

flame. At 60° the specimen of plastic sulphur became dull and cloudy in appearance, at 90° it regained its transparency, at 102° it began to show signs of flowing, and at 115° it was completely liquid. Another effect of the heat was to deepen the color slightly, so that in the liquid state this specimen had about the same color as an equal amount of N/10 iodine solution. The specimen of orthorhombic sulphur began to melt at 115°, and was completely molten at 120°. It gave a light, amber colored liquid, having a slight greenish tint. The difference in the color of the two specimens was certainly very marked. The flame was now removed and the bath allowed to cool slowly. As was to be expected, the liquid resulting from the melting of the orthorhombic sulphur crystallized first at 78°, whereas the melt from the plastic sulphur did not crystallize until 63° was reached. The flame was again placed under the bath and the tubes reheated. The tube which originally contained the plastic sulphur began to show signs of melting at 107° and was completely molten at 110°. The original orthorhombic specimen now began to melt at 114° and was completely fused at 120°. In the liquid condition each specimen assumed very nearly the same tint as before. On gradual cooling, the specimen resulting from the melting of the orthorhombic variety crystallized at 95°, whereas that resulting from the plastic form crystallized at 80°. Heat was reapplied. The plastic specimen melted at from 113° to 115°, the orthorhombic at 116°. As the result of these successive heatings the two specimens were beginning to show an alteration in color. The original plastic specimen was becoming perceptibly lighter in color, whereas the original orthorhombic specimen was beginning to take on a reddish-brown tint. It therefore occurred to us that if the two specimens were heated for a sufficient length of time they would become alike in color. Accordingly, the two tubes were heated for about five hours at 120° to 125°. At the end of this time both specimens were reddish-brown in color and were practically of the same tint. It is evident, therefore, that whether we start with plastic or orthorhombic sulphur, a chemical equilibrium

is ultimately reached as the result of the application of heat to the system.

On the Effect of Tension on the Crystallization of Plastic Sulphur.

It is a matter of common observation that stretching or handling plastic sulphur has a tendency to accelerate its crystallization. This is doubtless the result both of the action of heat and mechanical disturbance. It seemed of interest, therefore, to determine the effect of tension on the crystallization of the substance. Several experiments having this for their object were carried out in this laboratory by Mr. Bassett several years ago. Strands of plastic sulphur of about equal length, were cut from the same piece, and pieces of thin rubber were tied to the ends of the pieces of plastic sulphur. In one case the rubber ends were drawn taut over upright pins, inserted in a block of wood in such a way as to exert considerable tension on the strand of plastic sulphur with which they were connected, whereas the rubber end-pieces connecting the second strand of sulphur were left free and hence exercised no tension on the second strand of plastic sulphur. Both pieces were kept under water during the interval of the experiment. After the lapse of several hours the two pieces of sulphur were removed from the water and disconnected from the rubber strands. They were then dried and weighed, and the amount of soluble sulphur determined in each by bringing them in contact with carbon bisulphide, and weighing the insoluble residue. The following results were obtained:

Experiment 1.

	Per cent of soluble sulphur found.
Plastic sulphur poured at 300°:	
Under tension	55.13
Not under tension	31.71

Experiment 2.

	Per cent of soluble sulphur found.
Plastic sulphur poured at 350°:	
Under tension	45.24
Not under tension	21.20

In harmony with these results it was invariably found that the specimens of sulphur under tension became brittle, opaque, and crystalline, whereas the strands not under tension remained plastic and translucent during the interval of the experiment.

An interesting confirmation of these results has recently been obtained. Beautifully transparent strands of plastic sulphur were prepared by carefully pouring sulphur that had been heated to 250° into cold water. The strands had an even thickness of about $\frac{1}{4}$ inch. Two of them were cut into lengths of 2 inches each and clamped at the ends by means of delicate rubber clamps. One of them was drawn out so as to increase the original length by about $\frac{1}{2}$ inch, whereas the other was left free. The former, therefore, was under considerable tension whereas the latter was not. Both were kept side by side under water during the experiment. Both remained perfectly clear and transparent for some time. At the end of one and one-half hours, however, relatively large, well-defined crystals began to develop in the longitudinal axis of the strand under tension, whereas the strand not under tension remained perfectly clear and transparent, showing no crystallization whatsoever. At the end of two hours the crystallization had extended almost throughout the piece under tension, whereas in the specimen not under tension only a few crystals were to be seen. The specific gravities of the two pieces were then determined with the following results:

Initial specific gravity	1.94
Specific gravity specimen, not under tension	1.953
Specific gravity specimen, under tension	1.975

The phenomena here under consideration are doubtless altogether analogous to the changes which take place in metals when the latter are subjected to mechanical stress.

The Dilatometric Method of Measuring the Rate of Change of Plastic into Crystalline Sulphur.

Kopp[1] seems to have been the first to employ the dilatome-

[1] Ann. Chem. (Liebig), **93**, 129-232 (1855).

ter in measuring the change of volume of sulphur and various other substances produced by heating and melting. More recently Reicher,[1] working in van 't Hoff's laboratory, has employed this instrument in determining the transition temperature of sulphur, and in studying the change of the orthorhombic into the monoclinic variety. The interesting results obtained by these observers naturally suggested that possibly the dilatometer might be employed advantageously in determining the rate of crystallization of plastic sulphur.

Several simple forms of the instrument have been employed. One of these was constructed in the following manner: A 50 cc. pipette was fused off near the lower part of the bulb. The upper tube of the pipette was cut off about 1.5 inches from the bulb. The bulb was then filled with water and the required amount of freshly prepared plastic sulphur introduced. The bulb of the apparatus was connected with a millimeter tube, graduated in millimeters, about 2 feet long, by means of a tightly fitting rubber tube. By pushing the graduated tube into the bulb and carefully drawing it out again the column of water in the graduated tube could be adjusted to any desired height. In order to guard against leakage the rubber connection was carefully wrapped with copper wire, and as a further safeguard, the whole connection was covered over with black rubber tire-tape. The bulb of the apparatus was then immersed in water above the level of the rubber connection and the whole apparatus clamped in a vertical position. The gradual fall in the column of water in the millimeter-tube served to indicate the progress of the change, the height of the column being read off at different intervals. The graduated tube was accurately calibrated by means of mercury. The following are some of the results obtained with this form of apparatus:

Experiment 1.

Plastic sulphur poured at 440°.
Amount of sulphur used, 6.8295 grams.
Initial specific gravity of sulphur, 1.923.

[1] "Études de Dynamique Chimique," van 't Hoff: Eng. Trans., p. 94–95 (1896).

Specific gravity of sulphur when removed from dilatometer, 2.00.

Cubic capacity of dilatometer-tube per centimeter, 0.01319 cc.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	5.6	0	22.5	0
5	6.7	1.1	22.5	0.014509
5	8.7	1.0	22.5	0.01319
5	9.55	0.85	22.5	0.011211
5	10.15	0.6	22.5	0.007914
5	10.5	0.45	22.5	0.005935
5	10.9	0.4	22.5	0.005276
5	11.1	0.2	22.5	0.002638
5	11.3	0.2	22.5	0.002638
5	11.5	0.2	22.5	0.002638
5	11.7	0.2	22.5	0.002638
5	11.85	0.15	22.5	0.001978
5	12.0	0.15	22.75	0.001978
5	12.15	0.15	22.75	0.001978
5	12.2	0.05	23.0	0.000659
5	12.4	0.2	23.0	0.002638
5	12.45	0.05	23.5	0.000659
230	15.9	3.45	22.5	0.045505

Total contraction, 10.3 cm.

Contraction found by dilatometer, 0.1358 cc.

Contraction calculated from difference in specific gravity, 0.1365 cc.

Experiment 2.

Plastic sulphur poured at 250°.

Amount of sulphur used, 4 grams.

Initial specific gravity of sulphur, 1.931.

Specific gravity of sulphur when removed from dilatometer, 2.059.

Capacity of dilatometer tube, 0.01241 cc. per cm.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	6.7	0	21	0
3	7.65	0.95	21	0.01188
5	8.075	0.425	21	0.00527
5	8.4	0.325	21	0.00403
5	8.7	0.3	21	0.00372
5	8.95	0.25	21	0.00310
5	9.2	0.25	21	0.00310
5	9.45	0.25	21	0.00310
15	10.05	0.6	21	0.00744
15	10.6	0.55	21	0.00682
15	11.05	0.45	21	0.00568
15	11.45	0.4	21	0.00496
15	11.07	0.25	21	0.00310
945	17.05	5.35	21	0.06649

Total contraction, 10.35 cm.

Contraction found by dilatometer, 0.1284 cc.

Contraction calculated from difference in specific gravity, 0.1288 cc.

A comparison of the readings obtained in the first and second experiments of this series brings out, in a very striking way, the most essential difference between plastic sulphur prepared by pouring sulphur that has been heated only to moderately high temperatures, and that which has been prepared by pouring at temperatures in the vicinity of its boiling-point. A large part of the former always crystallizes almost immediately, whereas in the latter crystallization always proceeds with extreme slowness. The results obtained with the dilatometer therefore simply tend to confirm those of common experience.

With the form of dilatometer first employed, considerable difficulty was experienced on account of the narrow opening of the bulb of the instrument, and the difficulty of introducing the plastic sulphur with sufficient rapidity to avoid crystallization, after the determination of its initial specific gravity. With the view of overcoming this difficulty, recourse was had to the simple form of dilatometer proposed by Kopp.[1] As

[1] See drawing: Ann. Chem. (Liebig), 93, Fig. II. at end of volume.

made by us, the bulb of the instrument consisted of a wide-mouthed homeopathic vial, of about 1 ounce capacity. This was connected to the graduated millimeter-tube by means of a soft perforated cork, which had previously been boiled in oil, in order to render it impervious to water. The wide mouth of the bottle enabled us to introduce the sulphur into the apparatus with great rapidity, so that no time was lost in setting up the apparatus. The height of the column of water in the dilatometer-tube was adjusted to the desired level by alternately pushing in and withdrawing the tube. During the experiment the bulb of the apparatus was immersed in oil above the level of the cork. The following are the results of some experiments that were carried out by means of this instrument:

Experiment 3.

Plastic sulphur poured at 250°.

Amount of sulphur used, 14.6800 grams.

Initial specific gravity of sulphur, 1.901.

Specific gravity of sulphur when removed from dilatometer, 1.941.

Capacity of dilatometer-tube, 0.01319 cc. per cm.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	1.2	0	20	0
5	2.5	1.3	20	0.017147
5	3.8	1.3	20	0.017147
5	5.0	1.2	20	0.015828
5	5.8	0.8	20	0.010452
5	6.45	0.65	20	0.008573
5	7.0	0.55	20	0.007254
6.5	7.4	0.4	20	0.005276
5	7.75	0.35	20	0.004616
5	8.0	0.25	20	0.003295
5	8.3	0.3	20	0.003957
5	8.525	0.225	20	0.0029677
5	8.75	0.225	20	0.002967
5	8.975	0.225	20	0.002967
5	9.175	0.2	20	0.002638
5	9.375	0.2	20	0.002638

Dilatometer Readings (Continued).

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
5	9.575	0.2	20	0.002638
5	9.75	0.175	20	0.002308
5	9.95	0.2	20	0.002638
5	10.15	0.2	20.25	0.002638
5	10.45	0.3	20.25	0.003957
5	10.55	0.1	20.25	0.001319
5	10.775	0.225	20.25	0.002967
5	11.15	0.375	20.25	0.004946
5	11.325	0.175	20.25	0.002308
5	11.5	0.175	20.5	0.002308
5	11.7	0.2	20.5	0.002638
5	11.875	0.175	20.5	0.002308
5	12.05	0.175	20.5	0.002308
5	12.2	0.15	20.5	0.001978
5	12.45	0.25	20.5	0.001648
5	12.525	0.075	20.5	0.000989
5	12.7	0.175	20.5	0.002308
5	12.825	0.125	20.5	0.001648
5	12.975	0.15	20.5	0.001978
5	13.1	0.125	20.5	0.001648
17	13.5	0.4	20.5	0.005276

Total contraction, 12.3 cm.

Contraction found by dilatometer, 0.16225 cc.

Contraction calculated from difference in specific gravity, 0.16001 cc.

Experiment 4.

Plastic sulphur poured at 230°.

Amount of sulphur used, 8.4420 grams.

Initial specific gravity of sulphur, 1.911.

Specific gravity of sulphur when removed from dilatometer, 1.972.

Capacity of dilatometer tube, 0.01412 cc. per cm.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	2.4	0	20	0
5	4.4	2.0	20	0.02824
5	5.45	1.05	20	0.014826
5	6.05	0.6	20	0.008472
5	6.5	0.45	20	0.006354

Dilatometer Readings (Continued).

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
5	6.875	0.375	20	0.005295
5	7.175	0.3	20	0.004236
10	7.625	0.45	20	0.006354
5	7.825	0.2	20	0.002824
5	7.975	0.15	20	0.002118
25	8.575	0.6	20	0.008472
15	8.875	0.3	20	0.004236
5	8.925	0.05	20	0.000706
5	9.00	0.075	20	0.001059
11	9.15	0.15	20	0.002118
9	9.3	0.15	20	0.002118
35	9.85	0.55	20	0.00713
100	11.3	1.45	20	0.020474
15	11.5	0.2	20	0.002824
105	12.6	1.1	20	0.015532

Total contraction, 10.2 cm.

Contraction found by dilatometer, 0.1440 cc.

Contraction calculated from difference in specific gravity, 0.1365 cc.

Experiment 5.

Plastic sulphur poured at 220°.

Amount of sulphur used, 20.6900 grams.

Initial specific gravity of sulphur, 1.884.

Specific gravity of sulphur when removed from dilatometer, 1.934.

Capacity of dilatometer tube, 0.01412 cc. per cm.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	1.0	0	20	0
1	1.6	0.6	20	0.008472
1	2.15	0.5	20	0.007060
1	2.45	0.3	20	0.004236
1	3.0	0.55	20	0.007766
1	3.55	0.55	20	0.007766
1	4.05	0.5	20	0.007060
1	5.025	0.475	20	0.006707
1	5.5	0.475	19.75	0.006707
1	5.925	0.425	19.75	0.006001

Dilatometer Readings (Continued).

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
1	6.375	0.45	19.75	0.006154
1	6.725	0.35	19.75	0.004942
1	7.15	0.425	19.75	0.006001
1	7.525	0.375	19.75	0.005295
1	7.875	0.35	19.75	0.004942
1	8.25	0.375	19.75	0.005295
1	8.625	0.375	19.75	0.005295
1	8.925	0.3	19.75	0.004236
1	9.25	0.325	19.75	0.004588
1	9.505	0.255	19.75	0.0036
1	9.875	0.37	19.75	0.005224
1	10.15	0.275	19.75	0.003883
1	10.4	0.25	19.75	0.00353
1	10.65	0.15	19.75	0.002118
1	10.95	0.3	19.75	0.004236
1	11.2	0.25	19.75	0.003530
1	11.4	0.2	20	0.002824
1	11.65	0.25	20	0.00353
1	11.85	0.2	20	0.002824
1	12.05	0.2	20	0.002824
1	12.275	0.225	20	0.003177
1	12.45	0.175	20	0.002477
1	12.65	0.2	20	0.002824
1	12.825	0.175	20	0.002471
1	13.0	0.175	20	0.002471
1	13.2	0.2	20	0.002824
1	13.35	0.15	20	0.002118
1	13.6	0.25	20	0.003530
1	13.675	0.075	20	0.001059
1	13.8	0.125	20	0.001765
1	13.95	0.15	20	0.002118
1	14.1	0.15	20	0.002118
1	14.25	0.15	20	0.001765
1	14.375	0.125	20	0.001765
1	14.0	0.125	20	0.001765
1	14.62	0.12	20	0.001694
1	14.75	0.13	20	0.001835
1	14.875	0.125	20	0.001765
1	15.0	0.125	20	0.001765
1	15.1	0.1	20	0.001412
1	15.225	0.125	20	0.001765
1	15.325	0.1	20	0.001412

Dilatometer Readings (Continued).

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
1	15.425	0.1	20	0.001412
1	15.525	0.1	20	0.001412
1	15.625	0.1	20	0.001412
1	15.7	0.075	20	0.001059
1	15.8	0.1	20	0.001412
1	15.9	0.1	20	0.001412
1	16.0	0.1	20	0.001412
1	16.075	0.075	20	0.001059
3	16.5	0.25	20	0.00353
5	16.85	0.35	20	0.004942
5	17.225	0.275	20	0.003883
5	17.55	0.325	20	0.004588
5	17.85	0.3	20	0.004236
5	18.15	0.3	20	0.004236
5	18.4	0.25	20	0.00353
5	18.65	0.25	20	0.00353
5	18.9	0.25	20	0.00353
5	19.15	0.25	20	0.00353
5	19.4	0.25	20	0.00353
5	19.265	0.225	20	0.003177
5	19.825	0.2	20	0.002824
5	20.025	0.2	20	0.002824
5	20.225	0.2	20	0.002824
5	20.425	0.2	20	0.002824
5	20.6	0.175	20	0.002471
5	20.775	0.175	20	0.002471
5	20.95	0.175	20	0.002471

Total contraction, 19.95 cm.

Contraction found by dilatometer, 0.2815 cc.

Contraction calculated from difference in specific gravity, 0.2834 cc.

For successive intervals of five minutes the contractions show a gradual decrease. On the supposition that the change under consideration is a monomolecular process we have the following values for the coefficient of velocity :

Time. Minutes.	Contractions. cm.	Per cent of change.	*k*.
5	2.55	17.7	0.030288
10	2.375	24.6	0.029781
15	1.95	34.4	0.029103
20	1.63	42.6	0.028492
25	1.445	49.8	0.028190
30	1.10	55.3	0.027350

It will be seen from these numbers that there is a falling off in the velocity of the change, amounting to about 10 per cent, in thirty minutes. This gradual diminution in the rate of crystallization of plastic sulphur is in harmony with the conception that in this supercooled liquid we have to deal not with one, but probably with several molecular species, some of which pass to the crystalline variety of the element more rapidly than others. We have seen that such a conception derives support from various other properties of the substance such as the color, solubility in carbon bisulphide, etc.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, June, 1904.

PERCHROMIC ACID AND THE PERCHROMATES.[1]

BY HORACE G. BYERS[2] AND E. EMMET REID.[3]

HISTORICAL.

The well-known blue compound, formed when solutions of chromic acid or acidified chromates are treated with hydrogen peroxide, was discovered by Barreswill[4] in 1847 and is in common use as a means of detection of both chromic acid and hydrogen peroxide because of the intense blue color of its solution in ether, in which it is comparatively stable. The discoverer assigned to this compound the formula Cr_2O_7, because of the volume of oxygen evolved by it when reacting with hydrogen peroxide. He was unable to obtain any stable compounds of alkalies with it, nor was he able to isolate the substance giving rise to the blue color.

Fairly,[5] by similar means, deduced the formula CrO_6 for the blue substance.

Moissan[6] obtained the blue compound from the ethereal solution by rapid evaporation at —20° as an oily liquid, and showed that in this condition it evolved hydrogen by action on sodium amalgam. From the amount of oxygen which the

[1] This work was begun at the University of Washington and continued, jointly, at the University of Chicago, in the laboratory of General and Physical Chemistry.
[2] University of Washington.
[3] Baylor University, Texas.
[4] Ann. chim. phys., [3], 20, 2641.
[5] Chem. News, 33, 237.
[6] Compt. rend., 97, 96.

blue solution evolved by its spontaneous decomposition in the presence of alkalies, he concluded that the blue substance has the composition $CrO_4.H_2O_2$. He states that by its action on the alkali metals chromates are produced.

Berthelot,[1] studying the compound from the point of view of the oxygen evolved when acidified bichromates are treated with hydrogen peroxide, assigns to the blue compound the probable formula $H.CrO_4.H_2O_2$.

Pechard,[2] by treatment of the aqueous solution of the blue compound with barium hydroxide, obtained a compound to which he assigns the formula $BaCrO_5$.

Hausserman,[3] by treatment of chromium hydroxide with sodium peroxide, obtained a compound to which he assigns the formula $Na_8Cr_2O_{15}.28-30H_2O$.

Wiede[4] prepared from the blue ethereal solution a salt to which he gave the composition $(NH_4)_3CrO_4$, and a series of salts of the organic bases to which he assigns the general formula $RCrO_5$. He also prepared the salts of ammonium, sodium, and potassium, and assigns to these the composition expressed by the formula $MCrO_6H_2O_2$. He concludes, therefore, that the blue solution contains chromium in the state of oxidation implied by the formula Cr_2O_9.

Patten,[5] by reason of the color produced when the blue aqueous solution is treated with a solution of sodium acetate, and because of a purple precipitate formed when the ethereal solution is treated with solid sodium acetate, concludes that the blue solution contains chromium in the state of oxidation conforming to the oxide CrO.

A study of the foregoing literature convinced the authors of the present paper that more work on this subject is desirable, and that the many attempts to get compounds of the blue substance by direct treatment with the alkali metals failed only by reason of the temperature at which these attempts were made. The following investigation resulted:

[1] Compt. rend., **108**, 25; **157**, 477.
[2] *Ibid.*, **113**, 39.
[3] J. prakt. Chem., **48**, 70.
[4] Ber. d. chem. Ges., **30**, 2178; **31**, 516, 3139; **32**, 378.
[5] This JOURNAL, **29**, 385 (1903).

EXPERIMENTAL.

The Potassium Salt.—Acting on the hypothesis that the formation of chromates by the action of alkalies and the alkali metals is due to the decomposition of the product first formed, the blue solution was prepared, using an acidified bichromate solution saturated at the ordinary temperature of the room, and just sufficient 2.5 per cent hydrogen peroxide to give the supernatant layer of ether an intense blue color. This blue solution was cooled to about —20° and freshly cut pieces of potassium dropped in. The low temperature was maintained by the use of solid carbon dioxide, which was placed in an ether-bath surrounding the blue solution or was dropped directly into the latter. A vigorous evolution of gas, which was proved by analysis to be hydrogen, followed the addition of the potassium. At the same time there was produced a purplish-black precipitate, and the blue solution was ultimately decolorized. This precipitate quickly decomposes, when exposed to the air at the room temperature, with the evolution of oxygen and the formation of a substance which proved to be the bichromate. It dissolves in water with the formation of a sherry wine color, and, if the water is ice-cold, only slowly fades to the color of the chromate. It regenerates the blue color when acidified in the presence of ether.

As the compound seems to begin to decompose even below zero the analysis by the usual methods is difficult. Since the compound evolves oxygen on decomposition and forms a dichromate, it was thought that the determination of the available oxygen would be a means of arriving at the composition.

A N/10 solution of potassium bichromate was titrated against a neutral solution of ferrous ammonium sulphate of similar concentration. Measured quantities of the latter, usually 50 cc., were diluted with about 100 cc. of recently boiled water. In the earlier experiments ordinary distilled water was used. Into the iron solution, portions of the potassium salt were dropped, and the solution vigorously stirred. The portions used were washed with cold ether, and care was

taken to insure a large excess of iron. The solution was acidified with sulphuric acid and the excess of iron determined by titration against the bichromate solution, using ferricyanide as an indicator.

The titrated solution was then made alkaline with ammonia, boiled, and filtered. The precipitated hydroxides of iron and chromium were dried and fused in an iron crucible with an excess of sodium peroxide and a small piece of potassium hydroxide over a Bunsen burner. The fused mass was dissolved in water, saturated with carbon dioxide, and filtered. The residue was again fused and redissolved. The two solutions were titrated against the iron solution. These titrations give, in the first instance, the oxidizing power of the potassium salt, and in the second, the oxidizing power of its chromium in the known form of the chromate. Of course, deduction was made for the amount of chromium introduced in the first titration.

The following results were obtained, the oxidizing power being expressed in terms of cubic centimeters of N/10 bichromate. The ratio given in the tables is based on the following considerations: In the iron solution, when acidified, the chromates are reduced to the state of oxidation represented by the oxide Cr_2O_3. In the case of the chromate this is represented by $2CrO_3 \rightarrow Cr_2O_3 + 3O$. If the state of oxidation of the chromium in the blue compound corresponds to the oxide Cr_2O_7 the relation would be:

$$Cr_2O_7 \rightarrow Cr_2O_3 + 4O.$$

The ratio of the available oxygen would then be 4 : 3.

Table I.

	Salt solution. cc.	Chromate solution. cc.	Ratio.
1	50.5	39.5	3.84 : 3
2	27.4	19.4	4.24 : 3
3	27.4	19.9	4.14 : 3
4	34.1	25.4	4.03 : 3
5	29.5	21.75	4.07 : 3
		Mean,	4.065

A solution of potassium hydroxide in ether will also precipitate the potassium salt, and determination of the potas-

sium chromate ratio was made upon two samples of the partially dried salt so prepared, with the following results. The potassium was weighed as the sulphate and the chromium as the oxide:

Table II.

	Salt. mg.	Potassium.	Chromium.	Ratio of K : Cr.
1	122	24.6	34.4	1 : 1.38
2	127	27.3	37.7	1 : 1.39
			Calculated ratio,	1 : 1.33

Wiede[1] prepared, in the same way, a salt very similar in appearance to the one under investigation and ascribed to it the formula $KCrO_5.H_3O_2$. He also prepared his salt by precipitation of the blue solution with an alcoholic solution of potassium cyanide. In this salt he continually found the ratio of potassium to chromium as expressed above, but the oxygen values were higher than those obtained by us. He prepared his blue solution by use of a very large excess of hydrogen peroxide, 250 cc. of a 10 per cent solution with 10 grams of chromic anhydride.

It seemed probable that the difference in results is in some way connected with this excess of hydrogen peroxide. To test this point Wiede's salt was prepared, and instead of using his method of analysis the oxidizing power of the salt was determined as previously outlined. The result is given in Table III. The blue solution was then prepared without excess of hydrogen peroxide, and the additional precaution was taken of washing the solution twice with a chromic acid solution. The results in this case are given in Table IV.

Table III.

	Salt.	Chromate.	Ratio.
1	35.0	22.9	4.58 : 3
2	26.5	17.4	4.57 : 3
3	17.3	11.4	4.56 : 3
A second sample:			
1	37.3	24.10	4.66 : 3
2	35.15	22.11	4.77 : 3
3	29.85	19.9	4.49 : 3

[1] *Loc. cit.*

Table IV.

	Salt.	Chromate.	Ratio.
1	16.9	12.8	3.96 : 3
2	11.1	8.14	3.96 : 3
3	16.2	12.12	3.98 : 3

It seems possible that the large amounts of oxygen indicated in Table III. are due to cryoscopic hydrogen peroxide or to the formation of a compound of another series (see summary at close of article). An attempt was made to obtain a complete analysis of the potassium salt by the following method. Portions of the same sample of the potassium salt used in the analyses given in Table IV. were dropped into tubes, the lower, closed ends of which were surrounded with solid carbon dioxide. The upper ends were then sealed with a blast-lamp. Thus enclosed, the substance changes quietly into the bichromate. On opening these tubes, after weighing, considerable gas escaped and the odor of ether was plainly noticeable. Tubes 1 and 2 (see Table V.) were opened by breaking off the capillary tips by means of an iron rod passing through the stopper of a U-tube in which they were successively placed. The U-tube was immersed in a boiling salt solution and the water from the tubes driven over into weighed calcium chloride tubes by means of carbon dioxide. In tubes 3 and 4 the moisture was determined by weighing the tubes after opening and again after heating to 140° in an air-bath. The contents of each tube were washed into a platinum dish and titrated with the iron solution, the chromium and iron precipitated, and the potassium determined as the sulphate. The chromium precipitate was fused and determined as usual. The results follow. The excess of potassium in 1 and 2 over that required for the bichromate is probably due to potassium cyanide or to potassium carbonate contained in the cyanide used.

Table V.

	I.	II.	III.	IV.
Total substance	70.5	57.9	....	49.17
Weight of gas	9.19	10.9	....	11.6
Weight of moisture	4.11	2.9	4.3	2.4
Weight of solid contents	56.5	44.1	55.3	35.7
Weight of bichromate (by titration)	52.9	40.5	53.18	33.19
Weight of bichromate (by fusion)	52.7	41.2	53.8	34.1
Potassium found	17.1	14.3	14.1	8.84
Calculated potassium (from bichromate found)	14.1	10.7	14.3	8.89

The above results make it clear that the substance yields pure potassium bichromate on spontaneous decomposition, and that the potassium and chromium are present in the same ratio as in the dichromate.

The Sodium Salt.—In the attempt to prepare the sodium salt in the same way as the potassium the difficulty was encountered that the compound which formed was closely adherent to the sodium, and was with difficulty separated from it. Particles of sodium caused trouble when the mass was put into the iron solution. The sodium salt thus prepared is similar in appearance to the potassium salt, but appears to decompose more easily, and at temperatures approaching zero assumes a pasty form. Analysis number 1, given in Table VI., is from the salt thus prepared.

It seemed probable that the substance prepared by Patten[1] is this sodium salt. With this in view the blue ethereal solution was prepared, cooled to —20°, and treated with powdered sodium acetate. A purple precipitate was formed mixed with the excess of acetate. The supernatant ether was found to contain acetic acid. It was shown by blank tests that the excess of acetate interfered in no way with our method of analysis. After decanting the ether and washing thoroughly with cold ether until the residue was free from the blue color, samples were analyzed with results appended:

[1] *Loc. cit.*

Table VI.

	Salt.	Chromate.	Ratio.
1	23.5	18.2	3.87 : 3
2	32.0	24.10	4.10 : 3
3	30.0	22.5	4.0 : 3
4	47.8	34.5	4.16 : 3
		Mean,	4.01 : 3

The Ammonium Salt.—An ammonium salt was prepared by passing gaseous ammonia into the blue ethereal solution cooled to about —40°. It is probably not necessary to work at such a low temperature, though one attempt to prepare the salt at —10° was without result. The salt is a brownish-yellow, and on analysis gave the results listed in Table VII. No attempt has yet been made to determine its relation to the salt prepared by Wiede and assigned the formula $(NH_3)_3CrO_4$:

Table VII.

	Salt.	Chromate.	Ratio.
1	31.5	23.0	4.11 : 3
2	32.7	23.7	4.14 : 3
3	33.3	24.12	4.13 : 3
		Mean,	4.13 : 3

Other Salts.—By using the acetates of lithium, magnesium, calcium, barium and zinc in the same way as in the case of the sodium, the corresponding salts of these metals were prepared. The magnesium and zinc salts acted only slowly upon the blue solution. All these compounds formed a chocolate-brown slurry with the excess of acetate and the ether used in washing. The analyses were carried out as in the other cases, except that in the case of the barium salt a solution of ferrous chloride was used as a reducing agent, and the solution was acidified with hydrochloric acid. All these compounds decomposed at the room temperature with the evolution of gas and the formation of yellow chromates. Table VIII. contains the results of the analyses:

Table VIII.

	Lithium salt.	Chromate.	Ratio.
1	10.7	8.1	3.98 : 3
2	17.4	12.7	4.10 : 3
		Mean,	4.04 : 3
	Magnesium salt.	Chromate.	Ratio.
1	17.2	13.1	3.94 : 3
	Calcium salt.	Chromate.	Ratio.
1	27.4	19.5	4.12 : 3
2	25.3	19.5	3.94 : 3
3	36.5	27.5	3.98 : 3
4	36.5	28.1	3.83 : 3
		Mean,	3.97 : 3
	Barium salt.	Chromate.	Ratio.
1	24.1	18.1	3.98 : 3
2	25.3	19.25	3.94 : 3
		Mean,	3.96 : 3
	Zinc salt.	Chromate.	Ratio.
1	9.0	6.5	4.15 : 3
2	10.0	7.4	4.05 : 3
		Mean,	4.10 : 3

The average ratio of the oxidizing power of all the salts to that of their chromium in the form of the chromate is 4.02 : 3.

These results point so clearly to the existence in the blue solution of an acid of the composition expressed by the formula $HCrO_4$ (or more probably $H_2Cr_2O_8$), that it was of interest to study the decomposition of the blue compound in the presence of alkalies.

The blue solution, prepared as in the previous experiments, was divided into four 50-cc. portions. One of these was evaporated to dryness in a platinum dish and the residue ignited and weighed as chromium oxide. The second and third were each placed in 250 cc. of recently boiled ice-cold water containing 50 cc. of the standard iron solution and shaken vigorously in a separatory funnel and the oxidizing power determined.

It was found that the ether interfered somewhat with the titration, by reason of surface phenomena, and hence a slight excess of the bichromate was added, and the solution boiled and cooled before completing the titration. The chromium was precipitated, fused, and redetermined as before. The fourth portion was placed in a Lunge nitrometer (capacity 150 cc.) with 60 cc. of dilute caustic soda, confined over mercury. After decomposition was complete the oxygen was determined by absorption in pyrogallol, after removal of the ether vapor. The alkaline solution was titrated against ferrous iron. Since several observers have shown, and as our own experience also shows, that there is a slight reduction below the bichromate stage of oxidation under these conditions, the chromium was reprecipitated and again determined after fusion. The results are given in Table IX.

Table IX.

1	Cr_2O_3 found 0.0738 gram, equivalent to 29.10 cc. N/10 bichromate.		
	Blue solution.	Chromate.	Ratio.
2	40.1	30.4	3.96 : 3
3	39.6	29.166	4.01 : 3
4	Volume of oxygen (corr.) 6.5 cc., equivalent to 11.61 cc. N/10 bichromate.		

The alkaline solution was found equivalent in oxidizing power to 27.5 cc. bichromate and after fusion to 29.54 cc.

From the literature it appears that most of those who have worked upon this solution have used a large excess of hydrogen peroxide over that needed to effect the state of oxidation here indicated. It was then of interest to see if the presence of a known excess of hydrogen peroxide would affect the nature of the blue solution.

The solution was prepared as before and afterward shaken with an excess of 2.5 per cent hydrogen peroxide The aqueous layer was separated, but the ether portion was not dehydrated. Portions of this solution were then analyzed as before. Fifty cc. of it contained 0.0682 gram of chromic oxide corresponding to 26.88 cc. N/10 bichromate. A second portion of 50 cc., decomposed in the nitrometer as before,

gave 10.05 cc. oxygen, equivalent to 17.96 cc. bichromate, while the re-fusion of the precipitated chromate showed itself equivalent to 22.1 cc. Hence the ratio of the oxidizing power of the blue solution to its equivalent chromate is as 5.44 : 3. A 50 cc. portion of the solution, titrated directly against the iron in the former manner, gave as the oxidizing power 62.9 cc., and in the form of the chromate a value of 29.3 cc.—a ratio of 6.4 : 3.

Attention is again called to the fact that this solution was not dehydrated, as that fact has perhaps a bearing on the question referred to in paragraph 3 of the summary.

Summary and Conclusions.

1. The experimental portion of this paper shows conclusively the existence of the perchromates and that they have the general formula $MCrO_4$, or $M_2Cr_2O_8$. The latter formula is perhaps more probable by reason of the analogous persulphates.

2. The blue solution, prepared without excess of hydrogen peroxide, contains the acid corresponding to these salts, *i. e.*, $H_2Cr_2O_8$.

3. The results obtained by Moissan, Pechard, and by us when using a solution prepared with an excess of hydrogen peroxide all point to the probable existence of another compound possessing higher oxidizing capacity. Whether this be true or not is a problem for which it is our hope to find the solution.

We are continuing this work and hope to be able to prepare other salts of this acid and to ascertain the relation of the acid and its salts to the other possible acids of chromium and its allied elements.

OBITUARY.

ALEXANDER WILLIAM WILLIAMSON.

The death of Professor Williamson, LL.D., F.R.S., on May 6th, removes one of the few remaining chemists on whose work the modern ideas of the science are based. Williamson

was born May 1, 1824, and had, therefore, just completed his eightieth year. After private preparation, he studied at the Universities of Heidelberg and Giessen, under Gmelin and Liebig, and afterwards for three years in Paris, working at the higher mathematics. In 1849 he was appointed Professor of Practical Chemistry at University College, London, with which institution he remained connected until his retirement, in 1887. Williamson's name will always be known in the history of chemistry on account of his work on etherification, 1850–1854. He showed quite clearly, and for the first time, the true relationship of the alcohols, ethers, and allied bodies to water, and formulated them on the "water type." This, and the subsequent proof afforded by Hofmann, that the amines belong to the "ammonia type" paved the way for the more general conceptions of valency. Williamson was also the first to suggest that there is a continuous process of interchange going on among the atoms composing the molecules of compounds.

CORNELIS ADRIAAN LOBRY DE BRUYN.

C. A. Lobry de Bruyn was born January 1, 1857, at Leenwarden, and died July 23rd, aged forty-seven years. Lobry de Bruyn studied at the University of Leiden, where he was assistant to Franchimont, and subsequently in Paris, under Würtz. In 1885 he was appointed chemist in the Dutch Marine Service, and in 1896 succeeded Gunning as professor at the University of Amsterdam. The work of Lobry de Bruyn which has attracted most attention is probably his isolation of free hydroxylamine in 1891, and of hydrazine in 1894. Both preparations depend on the use of methyl alcohol as solvent, and he studied its action on a number of other substances. A considerable portion of his activity was given to the investigation of the dinitrobenzenes, and he devoted much time to a study of the action of ammonia and dilute alkalies on the sugars. Good work was also done by him in analytical chemistry, and, during the later years of his life, he applied himself with increasing intensity to the solution of problems of general physical chemistry. He was elected a "Foreign Member" of the Chemical Society of London in the earlier part of the present year.

REVIEWS.

DIE CHEMIE DER ZUCKERARTEN. Von PROF. DR. EDMUND O. VON LIPPMANN, Direktor der Zuckerraffinerie Halle zu Halle a. S. Dritte völlig umgearbeitete Auflage. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1904.

The third edition of this comprehensive work brings the record of investigations up to February, 1904. It comprises in two "half" volumes 1912 pages of text, 39 pages of names of authors cited, and 50 pages of subject-index. The work is dedicated to the memory of Victor Meyer, the early teacher and later friend of the author.

The compilation of such a voluminous work requires an amount of labor almost appalling, which the author has indicated by a quotation from the "Carmina burana" of the thirteenth century:

> "Et ut opus faciant
> Quod non possit mori,
> Moriuntur studio,
> Subditi labori."

Happily, however, for the good of science this stupendous work has not exhausted his activities.

This book contains in compact form, logically arranged, practically everything that is known concerning the chemistry of the sugars. The author has also given all the relations of the sugars of a chemical, physical, and physiological character, as well as their significance for technology, agricultural chemistry, and food chemistry. The greatest possible brevity, consistent with exactness, completeness, and clearness of arrangement characterizes the work throughout.

In the logical arrangement of the work, the monosaccharides are the first treated, and the first "half" volume, of 1034 pages, is given up entirely to their study.

The second "half" volume treats of the sugars which are of the most economic and technical importance. Naturally, the chapter on sucrose or cane-sugar is the one which will attract the greatest attention in industrial quarters. This chapter comprises 388 pages.

Among the disaccharides maltose occupies the most prominent position, and 64 pages are given to the subject.

The trisaccharides occupy 50 pages and raffinose, naturally, is the most important of them from the point of view of applied chemistry.

The tetrasaccharides comprise, at the present time, only two, of which the more important is stachyose.

From the purely chemical standpoint, the fifth subdivision of the work is the most interesting. It treats of the construction, configuration, and synthesis of the sugars. In this division the remarkable work of the past few years in the synthesis of carbohydrates is intelligently set forth.

After the foregoing description of the character of the work it hardly need be said that this is a volume which no chemist interested in physiological or nutrition investigations can well do without. Those interested in theoretical study will also find the work of unusual significance, inasmuch as it sets forth the various theories which have been proposed in regard to the construction and relation of sugars in a clear and satisfactory manner.

A mere glance at the contents of the work shows, more than any words can, the immense strides which have been made in chemical investigations of this character in the past quarter of a century.

It is evident that the only method possible to keep chemists informed of the progress of their science is in the devoted work of specialists in bringing into comprehensive form all that is known of the subject under study.

If the chemistry of the sugars, arranged in the briefest possible statement of our knowledge, forms a volume of 2000 pages it is evident that, in its advance, the science of chemistry has outstripped the possibility of being known by any one human mind.

The author himself regrets the incompleteness of his work and the possibility of errors which may be therein contained. It was impossible to repeat even a small part of the experiments described by others, and in accepting the statements of their work and its conclusions he realizes that many inaccuracies may have crept into the book. This fault is fully recognized in the quotation he makes from LaRochefoucauld:

"Pour bien savoir les choses il en faut savoir le detail; et comme il est presque infini, nos connaissances sont toujours superficielles et imparfaites." H. W. W.

ANALYSE DES MATIÈRES ALIMENTARIES ET RECHERCHE DE LEURS FALSIFICATIONS. Par M. CH. GIRARD, Director du Laboratoire Municipal de Paris. Deuxième Édition Très Augmentée. Paris: Vve. Ch. Dunod, Éditeur. 1904. (Compiled under the direction of M. Chas. Girard by his assistants in the Municipal Laboratory.)

This is a volume of 849 pages devoted to the analysis of food-stuffs and methods of determining their adulterations. This work is largely the result of the experience of M. Chas. Girard, the director of the Municipal Laboratory of Paris.

A recognition of the food value of potable waters is found in the first part of the book, and 80 pages are devoted to that subject. The examinations described are bacteriological and chemical, giving in condensed form the methods of procedure in both cases. An interesting matter connected with the study of waters is the municipal ordinance in regard to the manufacture of ice for consumption. The first article of this ordinance forbids the manufacturer or storekeeper to sell, or place on sale for alimentary purposes, ice which does not give, by melting, potable water, that is, water fit for drinking both from the standpoint of the bacteria which it contains and its chemical composition.

The chapter on wines is naturally one of the most important in the book. It extends from page 81 to 205, inclusive, and is written by M. Sanglé Ferrière. In this chapter the mean composition of the leading varieties of French and foreign wines is given. The red wines of the Gironde, which is the most important of the wine-producing provinces, contain a mean percentage of alcohol, by volume, of 9.6. The white wines of the same class have a mean content of alcohol by volume of 10.1 per cent. The various forms of adulteration of wines are described. They consist chiefly in the adding of sugar to the musts deficient in saccharine matter, and in the mixing of wines made from pomace, to which sugar has also been added, with genuine wines. The different methods of treating wine are defined in full. Of special interest in this connection is the employment of fumes of sulphur to aid in the conservation of wine and in the clearing of white wines. The process of stopping the fermentation in wines is technically called "mutage," and the substances which are most employed in this process are sulphurous acid, alcohol, and salicylic acid. It is stated that the sulphurous acid used is obtained by burning sulphur matches, by the addition of alkaline bisulphites, or by the use of an aqueous solution of sulphurous acid. The Consulting Committee of Hygiene of France has condemned the practice of using salicylic acid in the above process, but condones this of sulphurous acid. Just why that distinction has been made does not appear clear from a hygienic point of view.

The article on the analysis of wines is written by M. Truchon and is an excellent summary of the processes now in use, many of which were devised or improved in the Municipal Laboratory.

The article on beer, extending from page 207 to 242, inclusive, is written by M. J. de Brevans. The definition of purity

is as follows: "Beer is an alcoholic drink obtained by the fermentation of infusions or decoctions of germinated barley flavored with hops." This definition excludes from the class of pure beer those varieties made by the fermentation of other cereal grains or of brewing sugars.

The chapter on cider is written by M. Sanglé Ferrière, and extends from page 243 to 262, inclusive. This article is of especial interest on account of the importance of the cider industry in Normandy and other parts of France. The article on vinegar extends from page 263 to 278, inclusive, and is also written by M. Sanglé Ferrière. Vinegar is defined as a product of the acetic fermentation of wine, or of any other alcoholic liquor. The word "vinegar," used in its strictly etymologic sense, can only be regarded as a product of the acetous fermentation of wine. Vinegar made from other sources, therefore, should be named to define their origin, namely, cider vinegar, malt vinegar, spirit vinegar, etc. Methods describing the technical and the analytical processes are complete and satisfactory.

The article on alcohol and spirits extends from page 279 to 352, inclusive, and is written by M. A. Saglier. The article opens with a brief historical sketch and afterwards a description of the different kinds of spirits in common use in France. Naturally, the most important of these beverages is brandy. The methods for the determination of the higher alcohols and the ethereal and aldehydic bodies derived therefrom during the aging of the brandy, are of particular value, and especially useful in this country in determining the purity of imported articles of this class.

The article on milk extends from page 353 to 399, inclusive; that on butter from page 401 to 438, inclusive; and the one on cheese from page 439 to 448, inclusive; all are by M. Ladan Bockairy. It is a remarkable fact that the quick commercial method of determining butter-fat in milk, devised by Babcock, which is entirely satisfactory for all ordinary purposes, is not even mentioned in this chapter.

Shorter articles on edible oils, lard, tallow, meats, cereals, fruits, coffee, tea, cocoa, chocolate, sugars, syrups, confections, preserves, spices, and coloring-matters are given on the same general plan as mentioned above. The analytical and technical discussions are quite full on all of these subjects, and in the main the methods of analysis described are those of most modern use and commonly employed in this country. In many cases, however, many changes in analytical methods, improvements, and even new methods developed in the Munici-

pal Laboratory are given in full. It is these parts of the analytical descriptions which will be found of most value to American readers.

The final chapter on the composition of playthings and the danger of poisoning the children therefrom, is written by M. Girard himself.

The work can be highly commended as of great value to all chemists engaged in the study of foods and the detection of adulterants therein, and in the execution of food laws.

H. W. W.

DIE RIECHSTOFFE. Von DR. GEORG COHN in Görlitz (Zugleich als VI. Band, 2 Gruppe. II. Abtheilung von *Bolley-Englers* Handbuch der chemischen Technologie). Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1904. 220 pp. Price, 6 marks.

The meaning of the word "Riechstoff" is given by the author as follows: "Ich nenne Riechstoffe natürlich vorkommende oder künstlich gewonnene, bei gewöhnlicher Temperatur flüchtige, chemisch einheitliche Körper, die vermöge ihres Geruches einer Anwendung im Haushalte des Menschen fähig sind. Riechstoffe im engeren Sinne sollen ausserdem die Eigenschaft haben, für den gebildeten normalen Menschen wohlriechend zu sein."

Nitrobenzene, discovered by Mitscherlich in 1834, is the first artificially prepared substance that came into use for the purpose of perfumery. Collas introduced it into commerce under the name "essence of mirbane," and in 1847 Mansfield prepared it by nitrating the benzene from coal-tar. About the year 1850 the esters of organic acids appeared on the English market as apple-oil, pear-oil, etc. In 1844 Cahours showed that methyl salicylate is the chief constituent of the oil of wintergreen. In 1868 Cahours discovered the preparation of benzoic aldehyde from benzal chloride. In 1875 coumarin was obtained synthetically by Perkin, and vanillin by Haarmann, and in 1888 "artificial musk" by Baur.

This book is of interest to the chemist, as it contains much valuable information and is suggestive. It deals with the literature of the subject, its history, the occurrence of the "Riechstoffe" in Nature, their preparation, their physical properties, their chemical conduct, and relations between odor and chemical constitution, the quantitative estimation of the "Riechstoffe," their physiological conduct, and their uses.

The author is of the opinion that the use of odoriferous substances will keep pace with the development of the industry, as has been the case with artificial dyes. "Perhaps," he says, "the maiden of the future will consider whether she

shall wear her ionone or her geraniol gown." It is to be hoped that she will not consider artificial or natural musk as desirable under any circumstances. I. R.

A COMPENDIUM OF CHEMISTRY, including General, Inorganic, and Organic Chemistry. By DR. CARL ARNOLD, Professor of Chemistry in the Royal Veterinary School of Hanover. Authorized translation from the eleventh enlarged and revised German edition by JOHN A. MANDEL, Sc.D., Professor of Chemistry, Physics, and Physiological Chemistry in the University and Bellevue Hospital Medical College. First edition, first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904.

It is to be expected that a book which has gone through eleven German editions will be worth translating into English. A great many useful facts and a large amount of chemical information are crowded into its pages, so that it may well serve as a convenient handbook for students and others who are unable to obtain larger works. In the opinion of the reviewer, it excels in this respect rather than as a text-book. It is evident that a book of less than 600 pages, which covers the ground of general, inorganic, and organic chemistry must be greatly condensed, and can devote but little space to the fundamental theories and generalizations of chemistry, and still less to the hundreds of substances mentioned. There are no descriptions of experiments, though under each element are given the principal tests for it.

The book is undoubtedly reliable in statement, and it contains an excellent index. C. E. W.